SUBSTITUTION CHEMISTRY OF THE COBALT COMPLEXES $RCCo_3(CO)_9$ (R = H, CHO) WITH THE DIPHOSPHINE LIGAND 4,5-BIS(DIPHENYLPHOSPHINO)-4-CYCLOPENTEN-1,3-DIONE (BPCD). SYNTHESES, X-RAY STRUCTURES, AND REACTIVITY

Jie Liu, M.S.

Thesis Prepared for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS

December 2001

APPROVED:

Michael G. Richmond, Major Professor, Chair of Graduate Studies in Department of Chemistry
Oliver Chyan, Committee Member
Ruthanne D. Thomas, Chair of the Department of Chemistry
C. Neal Tate, Dean of the Robert B. Toulouse School of Graduate Studies

Liu, Jie, Substitution chemistry of the cobalt complexes $RCCo_3(CO)_9$ (R = H, CHO) with the diphosphine ligand: 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd). Syntheses, X-ray structures and reactivity. Master of Science (Chemistry), December 2001, 62 pp., 8 tables, 15 illustrations, reference list, 67 titles.

The reaction between the tetrahedrane cluster $RCCo_3(CO)_9$ {R = CHO (**1**), H (**3**)} and the redox-active diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) leads to the replacement of two CO groups and formation of $RCCo_3(CO)_7$(bpcd) {R = CHO (**2**), H (**4**)}. Clusters **2** and **4** are thermally unstable and readily transform into the new P-C bond cleavage cluster **5**. All three clusters **2**, **4**, and **5** have been isolated and fully characterized in solution by IR and ^{31}P NMR spectroscopy. VT ^{31}P NMR data indicate that the bpcd ligand in $RCCo_3(CO)_7$(bpcd) is fluxional at 187 K in THF. Clusters **2**, **4**, and **5** have been structurally characterized by X-ray diffraction analyses.

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Professor Michael G. Richmond for his kind guidance, never-ending encouragement, assistance in directing the described research, and serving as the chairman of my advisory committee. I am especially grateful to Dr. Richmond for his model role as a professor and researcher, his efforts in stressing new knowledge, and his insistence for academic excellence, all of which are benefits that will assist me in my future endeavors. Dr. William H. Watson is acknowledged for his assistance with all of the X-ray crystallographic structures. Dr. Oliver Chyan is thanked for serving on my advisory committee. The help given to me by my colleague, Dr. Jiancheng Wang, to whom I am grateful, is most appreciated.

The author is sincerely grateful to his parents and wife for their patience, encouragement, support and special love throughout the years.

Finally, I wish to thank the Department of Chemistry, University of North Texas, and the Robert A. Welch Foundation for financial support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

Chapter I Introduction

The chemistry of transition-metal complexes and their phosphine-substituted derivatives has been a rapidly developing area of research in recent years with applications in the areas of catalysis and material science.[1]

Our group is interested in clusters that allow for the study of the interaction between redox-active diphosphine ligands and polynuclear cluster compounds.[2] Whereas the activation of simple phosphine ligands by polynuclear cluster compounds has been extensively explored over the last several years, our current work has dealt with the thermal and catalyst-mediated substitution chemistry of ruthenium and cobalt clusters with the redox-active ligands bma and bpcd.[2, 3, 4, 5] Wishing to explore the effect of the capping ligand on the course of ligand substitution, coupled with our interest in producing clusters with multiple redox responses, we have investigated the reactivity of the H- and CHO-substituted cobalt clusters with bpcd.

In this thesis, two topics will be discussed: (1) ligand substitution reactions and the reversible chelate-to-bridge bpcd ligand exchange reactions in the tricobalt cluster $OHCCCo_3(CO)_7$(bpcd) [where bpcd = 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione], and (2) P-C bond cleavage reaction involving the bpcd-substituted complexes $OHCCCo_3(CO)_7$(bpcd) and $HCCo_3(CO)_7$ (bpcd).

A. Phosphine Ligands

Transition metals exhibit a pronounced tendency to form complexes with trivalent compounds of phosphorus.[6] Phosphines have been used widely in the field of organometallic chemistry because they appear to be extremely versatile in their ability to stabilize a wide variety of metals in a wide variety of oxidation states. By changing the substituent groups, one can alter the tertiary phosphine's ability to influence the activity, selectivity and stability of a catalytic system via electronic and/or steric considerations.

Phosphines have a lone-electron pair on the central atom that can be donated to metal. However, they are also π acceptors because of the empty d orbitals. In the case of the CO ligand, it has long been recognized that it is the π^* orbitals that accept electron density from the metal, while in the case of PR_3 ligands, it has been suggested that the σ^* orbital of the P-R bonds plays the role of an acceptor orbital (Figure 1.1).[7, 8] Figure 1.1 reveals that as the P group becomes more electron rich, the orbital that the R fragment uses to bond to phosphorus becomes more stable. This implies that σ^* orbital of the P-R bond also becomes more stable. At the same time, the phosphorus contribution to σ^* increases, so does the size of σ^* lobe that points toward the metal. Both of these factors make the σ^* more accessible for back donation. The order of increasing π-acceptor character is:

$$PMe_3 < PAr_3 < P(OMe)_3 < P(OAr)_3 < P(NR_2)_3 < PCl_3 < CO < PF_3$$

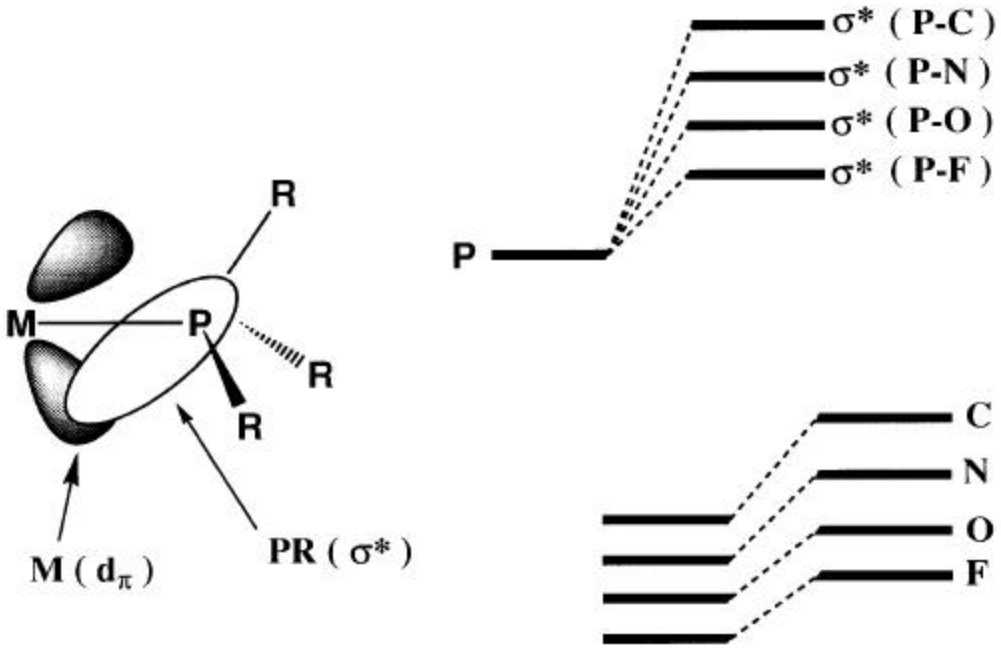


Figure 1.1 The σ* orbitals of the P-R bond play the acceptor role in metal complexes of phosphorus ligands. As the atom attached to phosphorus becomes more electronegative, the empty σ* orbitals of the P-X bond move to lower energy and become more accessible; the PX_3 molecule, therefore, becomes a better acceptor from the metal.

Tertiary phosphines are the most commonly encountered ancillary ligands associated with organotransition-metal compounds. The wide use of phosphine-substituted complexes occurs because they can alter product distributions in catalytic reactions and increase catalyst stability. Many investigations involving transition-metal carbonyl compounds have used phosphines (PR_3) as ligands because they constitute one of the few series of ligands in which the electronic and steric properties can be altered in

a systematic and predictable fashion over a wide range of R groups. Examples of monodentate, bidentate, tridentate and higher chelating phosphines are well documented in the literature.[6, 9, 10] A list of representative tertiary phosphines and related ligands is shown in Figure 1.2.

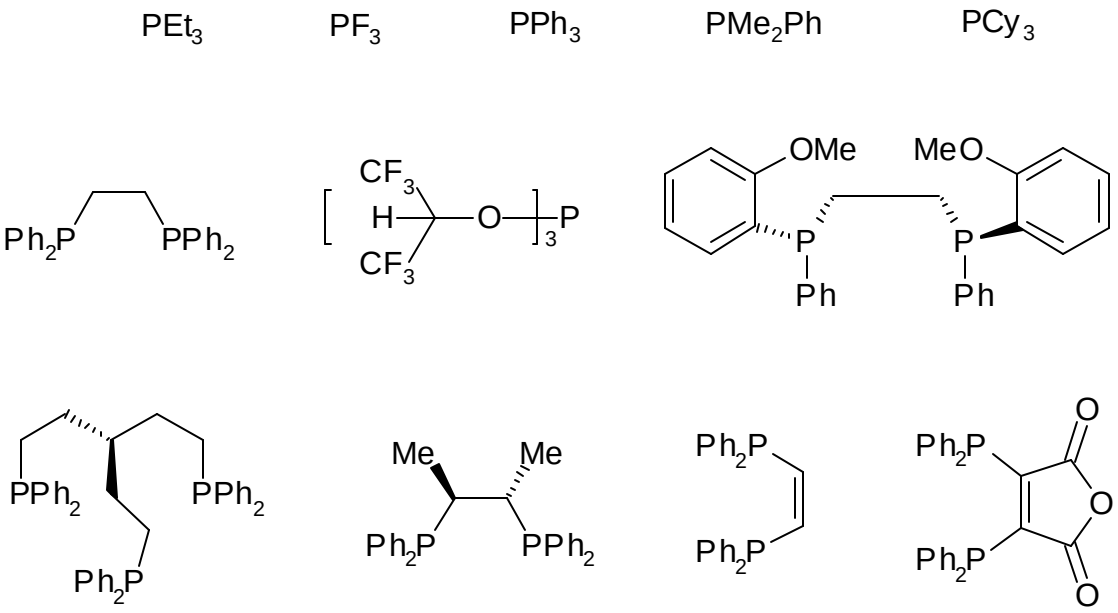


Figure1.2 Tertiary phosphines and related ligands

These ligands exhibit a wide range of steric and electronic effects. For example, PH_3 is very much smaller compared to PCy_3, whereas PF_3 and $(R_FO)_3P$ (R_F is any perfluoroalkyl) have sufficiently electron withdrawing substituents to act as strong π-acids, rivalving the coordination properties of the CO ligand. Bidentate phosphines such as diphos are also commonly employed and they generally lead to the formation of chelated five-membered ring complexes in the case of mononuclear systems. Chiral

phosphines are also known and they are very important as ligands in the asymmetric hydrogenation of prochiral olefins and other synthetic transformations involving asymmetic induction. Recently, water-soluble phosphines, such as sulfonated phosphines, have attracted the attention since water is a cheap and clean solvent.[11]

The electronic effects of tertiary phosphines depend markedly on the nature of the substitutent groups on phosphorus. Tertiary aliphatic and aromatic phosphines were once thought to stabilize transition-metal alkyl derivatives through $d\pi$-$d\pi$ backbonding in which filled metal d-orbitals interact with vacant d-orbitals on phosphorus. The possibility that π-backbonding is important in transition-metal complexes has been examined by using several physical chemical techniques (IR and NMR spectroscopy and X-ray crystallography) for a great variety of metal phosphine complexes in various oxidation states.[6] The dependence of the electronic effect of various PR_3 ligands on the nature of the R group has been quantified by Tolman,[12] who compared the ν(CO) frequencies of a series of complexes of the type $LNi(CO)_3$, containing different PR_3 ligands. The stronger donor phosphines increase the electron density on Ni, which passes some of this increased electron density along to the CO groups by π backbonding, which in turn lowers the ν(CO) of the $LNi(CO)_3$ complex.

The steric bulk of phosphine ligands is their most important structural property. Bulky tertiary phosphines such as triphenylphosphine distort the surrounding ligands and shield the metal, thus, markedly affecting the chemistry of phosphine-substituted metal complexes. Bulky phosphines also tend to bind *trans* to one another. The presence of several bulky phosphine ligands in the same metal coordination sphere can cause

deviations from an idealized coordination geometry, which facilitates ligand dissociation.[13] The effect of steric interactions on the structural and physical properties of phosphine complexes has been extensively reviewed by Tolman, who has quantified the steric effect of phosphines by using the concept of the cone angle. This is obtained by taking a space-filling model of the $M(PR_3)$ group, folding back the R substituents away from the metal as far as they will go, and measuring the apex of the cone at the metal.[6] Table 1.1 summarizes the cone angles of phosphine ligands.

Table 1.1 Cone angles of tertiary phosphine ligands

Phosphorus Ligands PR_3	Cone Angle Θ^o
PH_3	87
$P(OCH_2)_3CR$	101
PH_2Ph	101
PF_3	104
$P(OMe)_3$	107
PMe_3	118
PMe_2Ph	122
$PPh_2CH_2CH_2PPh_2$	123
PEt_3	132
PPh_3	145
$PPh_2(t\text{-}Bu)$	157
PCy_3	170
$PPh(t\text{-}Bu)_2$	170
$P(t\text{-}Bu)_3$	182
$P(C_6F_5)_3$	184
$P(mesityl)_3$	212

One must be cautious in the separation of steric and electronic effects since they are often interrelated in transition-metal phosphine complexes.

The use of ^{31}P NMR spectroscopy has proved to be the most important method for studying organometallic complexes.[14, 15] The ^{31}P nucleus has a spin of I = 1/2, is 100%

abundant, and displays moderate NMR sensitivity. ^{31}P NMR data are quite useful for fingerprinting compounds and for distinguishing between related compounds. For example, the size of different phosphine chelate rings can be accessed, and unidentate and bidentate coordination of diphosphines can be easily determined. Moreover, the stereochemistry of many metal-phosphine complexes can be deduced from the phosphorus-phosphorus coupling constants because *trans* phosphines display a larger coupling constant than *cis* phosphines. The ^{31}P NMR information from both chemical shift and coupling constants is often used to determine the geometry of many complexes.

B. Tricobalt Clusters $RCCo_3(CO)_9$

Cobalt is an element known from cobalt blue; cobalt also functions as a γ-ray irradiation source and is a component in special steels and magnetic materials. The element cobalt serves as the central element of vitamin B_{12} which is one of the indispensable human nutrients. Cobalt compounds have been widely studied since they are used widely in catalytic processes. For instance, cobalt compounds have been widely used in the catalysis of hydroformylation, carbonylation, and oligomerization.[16]

The basic compound for the synthesis of organocobalt compounds is $Co_2(CO)_8$, which is a coordinatively compound that satisfies the 18-electron rule. $Co_2(CO)_8$ is prepared by reducing cobalt acetate, cobalt hydroxide or cobalt oxalate with hydrogen and reaction of the cobalt metal with carbon monoxide. $Co_2(CO)_8$ is an orange crystalline material (mp 51°C) that ignites in air and is soluble in organic solvents. As $Co_2(CO)_8$

releases carbon monoxide at room temperature to yield $Co_4(CO)_{12}$, it should be stored at 0 ^oC or below and under an inert gas or carbon monoxide atmosphere.[17]

The tricobalt cluster $RCCo_3(CO)_9$ (Figure 1.3) is a well-known transition metal compound. They can be synthesized from $Co_2(CO)_8$.[17] The tetrahedral Co_3C unit is found in a large number of methinyltricobalt nonacarbonyls of the general formula $RCCo_3(CO)_9$ (R = halogen, alkyl, aryl, carboxyl, etc.).

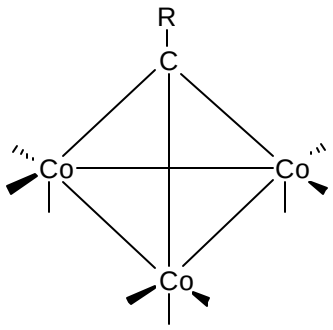


Figure 1.3 Structure of a μ_3-alkylidyne tricobaltnonacarbonyl cluster (R = halogen, alkyl, aryl, carboxyl, etc.)

In $RCCo_3(CO)_9$ clusters, six CO groups lie roughly equatorial with the remaining three CO groups positioned axially. The molecule possesses C_{3v} symmetry with the equatorial CO groups bent slightly out of the Co_3 plane toward the apical group. For compounds where the apical group does not introduce additional congestion in the molecule, the average dihedral angle between the tricobalt triangle and C-Co-Co triangle is thirty degrees. Robinson and coworkers[18] have shown that in $RCCo_3(CO)_9$ complexes there is extensive electron delocalization in the Co_3C tetrahedral unit and the reactivity of

the complex is governed by the substituent group(s) on the cobalt atoms and by the apical substituent. Ercoli and coworkers[19] found that the three axial CO groups exchange ^{14}CO faster than the equatorial CO groups. The relative rates were found to lie in the order R = H < Br < Cl < F. These data reveal that the apical group is involved in reactivity modulation, in a way similar to the *trans* effect in inorganic reactions.

The chemistry of the apical group arises from electronic and stereochemical aspects of the complexes. When the apical capping group is a halogen atom, there is sensitivity to nucleophilic attack and heterolytic cleavage of the C-R bond. This is why many simple derivatives of these types of complexes cannot be isolated, but instead yield dimerized compounds.[18] Physical features indicate properties consistent with an sp^3 carbon atom. This can be illustrated by viewing the core Co_3C as electron withdrawing with respect to apical group. The high electron density in the C-R group could be caused by polarization of the Co_3C core by a halogen atom or π-bonding.

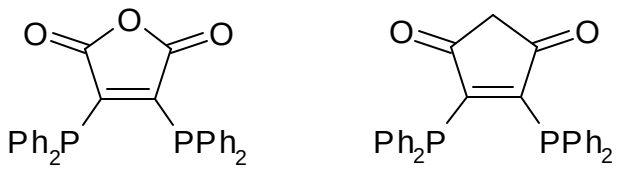
To study the electronic and stereochemical nature of these complexes, various mono- and bidentate phosphine derivatives have been made.[20] These ligands have been found to react reversibly with $RCCo_3(CO)_9$ (R = Cl, Br, CH_3, C_6H_5) to yield compounds of the general formula $RCCo_3(CO)_8L$ and $RCCo_3(CO)_7L_2$. These compounds are air stable, volatile and do not decompose in non-polar solvents. The stability associated with these compounds is derived from the ability of the $RCCo_3(CO)_9$ complex to act as an electron sink.[21] $RCCo_3(CO)_9$ clusters are generally considered congested compounds. The structures adopted by the phosphine-substituted clusters are those that minimize the

CO-CO interactions, which explains why equatorial substitution is observed despite the fact that apical group is distorted.

C. Ligand Substitution Reactions with Polydentate Phosphine Ligands

Polydentate-phosphine ligand substitution in the alkylidyne-bridged tricobalt clusters, $RCCo_3(CO)_9$, continues to be investigated in connection with hydroformylation catalysis, redox reactivity and NMR fluxionality studies. In these cases, the diphosphine ligand serves to bridge adjacent cobalt atoms via equatorial coordination.[21, 22, 23, 24, 25, 26, 27]

Our group has been interested in the substitution chemistry of tricobalt cluster compounds with polydentate phosphine ligands as a means to prevent or retard cluster fragmentation in electron-transfer reactions. We have studied the reactivity of polynuclear clusters with redox-active phosphines in an effort to prepare new ligand/cluster redox systems. It is our hope that such compounds will display superior electron reservior capabilities, as a result of the cooperative mixing of ligand and cluster orbitals.[2, 3, 4] The two redox-active diphosphine ligands that we have concentrated on are 2,3-bis(diphenylphosphino)maleic anhydride (bma) and 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd).



bma bpcd

Figure 1.4 Diphosphine ligands bma and bpcd

These two ligands that possess a low-lying π^* orbital that is delocalized over the five-membered ring display unique electronic properties in comparison to the common diphosphine ligands. An organometallic compound with this type of LUMO is expected to serve as an efficient electron reservoir by stabilizing electron counts in excess of 18 electrons.[28] Our goal is to study the possibility of producing new organometallic compounds that may exhibit long-range electronic communication due to intervalence transitions that may be triggered by absorption and/or a controlled change in the oxidation state of one of the redox-active sites by electrochemical activation.

These two particular diphosphines, first prepared by Becher and Fenske,[29] have been used as ligands in the syntheses and redox investigations of sundry mononuclear compounds by the same group. The bma ligand is unique on the basis of the work of Fenske,[30] and Tyler[31], who have demonstrated that this ligand assists in the stabilization of mononuclear 18 + δ complexes through electron delocalization with the low-lying π^* orbital of the phosphine ligand. Richmond[3] has reported the reaction between bma and $PhCCo_3(CO)_9$ leads to the substitution of two CO groups by the diphosphine ligand to afford the intermediate cluster $RCCo_3(CO)_7$(bma). This cluster loses CO upon

thermolysis or near-UV irradiation and undergoes an activation of the P-C (maleic anhydride) bond, coupled with reductive C-C bond formation between the capping-benzylidyne ligand and the transient Co-C (maleic anhydride) moiety to give the cluster $Co_3(CO)_6[\mu_2\text{-}\eta^2,\eta^1\text{-}C(Ph)C{=}C(PPh_2)C(O)OC(O)](\mu_2\text{-}PPh_2)$.

The phosphine ligand bpcd was first synthesized via reaction of 4,5-dichloro-4-cyclopenten-1,3-dione with diphenyl(trimethylsilyl)phosphine in 85% yield.[29] 4,5-Dichloro-4-cyclopenten-1,3-dione was prepared by first reducing hexachlorocyclopentadiene in the presence of zinc dust and hydrochloric acid to 1,2,3,4-tetrachlorocyclopentadiene.[32] Chlorination of the 1,2,3,4-tetrachlorocyclopentadiene gave 1,2,3,3,5,5-hexachloro-1-cyclopentene, while upon boiling the 1,2,3,3,5,5-hexachlorocyclopentene with concentrated sulfuric acid produced 4,5-dichloro-4-cyclopenten-1,3-dione as a colorless solid.[33]

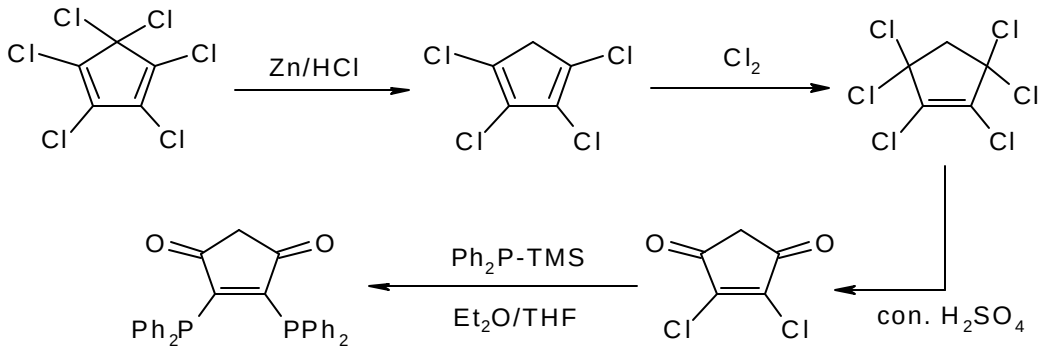


Figure 1.5 Synthetic route for bpcd

The research in our group has involved the reaction between the tricobalt clusters $RCCo_3(CO)_9$ (where R = Ph, ferrocenyl) and the ligand bpcd, which initially proceeds to

give the expected bpcd-substituted clusters $RCCo_3(CO)_7(\mu_2\text{-}PP)$. These clusters were subsequently shown to exhibit exceptional liability with respect to P-C bond scission, coupled with C-C bond reductive elimination to give $Co_3(CO)_6[\mu_2\text{-}\eta^2\text{:}\eta^1\text{-}C(R)C=C(PPh_2)C(O)CH_2C(O)](\mu_2\text{-}PPh_2)$. The work has been reported by our group and the coordination of the diphosphine ligand 4,5-bis(diphenylphosphino)-4-cyclopenten-1,3-dione (bpcd) to the tricobalt cluster $PhCCo_3(CO)_9$ affords the new cluster $PhCCo_3(CO)_7(bpcd)$,[5] which is thermally labile and transforms into $Co_3(CO)_6[\mu_2\text{-}\eta^2,\eta^1\text{-}C(Ph)C=C(PPh_2)C(O)CH_2C(O)](\mu_2\text{-}PPh_2)$. VT ^{31}P NMR data indicate that the bpcd ligand in $PhCCo_3(CO)_7(bpcd)$ is fluxional in solution, with two chelating and one bridging isomer being observed at 176 K in THF. The kinetics for the conversion of $PhCCo_3(CO)_7(bpcd)$ to $Co_3(CO)_6[\mu_2\text{-}\eta^2,\eta^1\text{-}C(Ph)C=C(PPh_2)C(O)CH_2C(O)](\mu_2\text{-}PPh_2)$ followed first-order kinetics in 1,2-dichloroethane (DCE). These data, coupled with the reaction rates being retarded in the presence of added CO, and the activation parameters support a scheme involving a dissociative CO loss as the rate-limiting step.

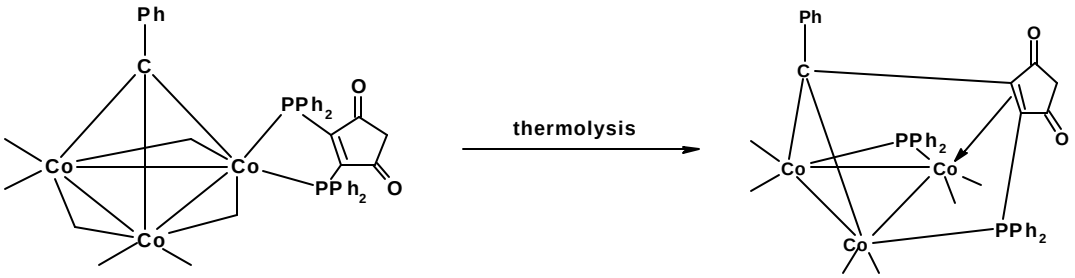


Figure 1.6 Thermal transformation of $PhCCo_3(CO)_7(bpcd)$

Wishing to explore the electronic and steric effects of the capping ligand on the course of ligand substitution reactions, we synthesized the H- and CHO-substituted tricobalt clusters in this thesis and studied their ligand substitution reactivities with bpcd.

Chapter References

1. Thimmappa, B. H. S. *Coord. Chem. Rev*. **1995**, 143, 1.
2. Shen, H.; Bott, S.G.; Richmond, M.G. *Inorg. Chim. Acta* **1996**, 241, 71.
3. Yang, K.; Bott, S. G.; Richmond, M.G. *Organometallics* **1995**, 14, 2718.
4. Xia, C.-G.; Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1996,** 15, 4480.
5. Bott, S. G.; Shen, H.; Richmond, M. G. *Struc. Chem.* **2001**, 12, 225.
6. Collman, J.P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *"Principles and Applications of Organotransition metal Chemistry."* University Science Books, Mill Valley, CA, **1987**, chapter 2.
7. Orpen, A.G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.
8. (a) Xiao, S.-X.; Trogler, W. C.; Ellis, D.E.; Berkovitch-Yellin, Z. J. *J. Am. Chem. Soc*. **1983**, 105, 7033. (b) Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, 29, 4167.
9. Clark, H. C. *Isr. J. Chem.* **1976/77**, 15, 210.
10. (a) Levason, W.; McAuliffe, C. A. *Acc. Chem. Res.* **1978**, 11, 363. (b) Levason, W.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1972**, 14, 173. (c) McAuliffe, C. A. *"Transition-Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands."* Wiley, New York, **1973**.
11. Darensbourg, D.; Bischoff, C. J. *Inorg. Chem.* **1993**, 32, 47.
12. Tolman, C.A. *Chem. Rev*. **1977**, 77, 313.

13. (a) Hitchcock, P. B.; McPartlin, M.; Mason, R. *Chem. Commun*. **1969**, 1367. (b) Bennett, M. J.; Donaldson, P. B. *Inorg.* Chem. **1977**, 16, 655.

14. Davies, J. A.; In *"The Chemistry of the Metal-Carbon Bond"* Hartley, F. R.; Ed; Wiley-Interscience, New York, **1982**, chapter 21, p880.

15. Pregosin, P. S.; Kunz, R. W. In *"NMR Basic Principles and Progress"* Springer-Verlag, Heidelberg, **1979**, Vol 16, p55.

16. Hegedus, L. S. *Coord. Chem. Rev*. **2000**, 204, 199.

17. Omae, I. *"Applications of Organometallic Compounds."* John Wiley & Sons, New York, NY, **1998**, Chapter 17.

18. Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res*. **1973**, 6, 73.

19. Cetin, G.; Ercoli, R.; Gambino, O.; Vaglio, G. *Atti. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Natur.* **1964**, 99, 1123.

20. Brice, M. D.; Penfold, B. R.; Robinson, W. T.; Taylor, S. R. *Inorg. Chem.* **1970**, 9, 1457.

21. Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc.* **1971**, A, 1457.

22. Balavoine, G.; Collin, J.; Bonnet, J. J.; Lavigne, G. *J. Organomet. Chem.* **1985**, 280, 429.

23. Collin, J.; Jossart, C.; Balavoine, G. *Organometallics* **1986**, 5, 203.

24. Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc.* **1982**, 104, 5633.

25. Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Rieger, P. H.; Williams, R. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442.

26. Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, 247, 321.

27. Sutin, K. A.; Kolig, J. W.; Mlekuz, M.; Bougeard, P.; Ssayer, B. G.; Quilliam, M. A.; Faggium, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *J. Organomet. Chem.* **1993**, 445, 163.

28. Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 2387.

29. (a) Fenske, D.; Becher, H. J. *Chem. Ber*. **1974**, 107, 117. (b) Fenske, D.; Becher, H. J. *Chem.. Ber*. **1975**, 108, 2115. (c) Fenske, D. *Chem. Ber.* **1979**, 112, 363.

30. (a) Becher, H. J.; Bensmann, W.; Fenske, D. *Chem. Ber.* **1977**, 110, 315. (b) Fenske, D. *Angew. Chem., Intl. Ed. Engl.* **1976**, 15, 381. (c) Bensmann, W.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 462. (d) Bensmann, W.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 677. (e) Fenske, D.; Christidis, A. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 129.

31. (a) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, 111, 130. (b) Mao, F.; Philbin, C. E.; Weakley, T. J. R.; Tyler, D. R. *Organometallics*, **1990**, 9, 1510. (c) Mao, F.; Sur, S. K.; Tyler, D. R. *Organometallics*, **1991**, 10, 419. (d) Mao, F.; Tyler, D. R.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 3113. (e) Tyler, D. R. *Acc. Chem. Res.* **1991**, 24, 325. (f) Mao, F.; Tyler, D. R.; Bruce, M. R. M.; Bruce, A. E.; Rieger, A. L.; Rieger, P. H. *J. Am. Chem. Soc.* **1992**, 114, 6418.

32. McBee, E. T.; Meyers, R. K.; Baranauckas, C. F. *J. Am. Chem. Soc.* **1955**, 77, 86.

33. Roedig, A.; Hörnig, L. *Chem. Ber.* **1955**, 88, 2003.

Chapter II Experimental

A. Materials

1. Solvents

CH_2Cl_2 was distilled from CaH_2. THF, Et_2O, and toluene were distilled from sodium/benzophenone ketyl. All distilled solvents were stored under argon in Schlenk vessels equipped with Teflon stopcocks.

2. Reagents

$Co_2(CO)_8$ was purchased from Strem Chemicals and used as received. $RCCo_3(CO)_9$ (R = CHO,[1] H[2]) were prepared by the procedures reported by Seyferth, and the bpcd ligand was synthesized by using the reported method.[3] n-BuLi (2.5 M in hexane) and Me_3NO were purchased from Aldrich and used as received. n-BuLi was titrated against diphenylacetic acid prior to use.[4]

B. Instrumentation

All reactions were conducted under argon using Schlenk techniques. Routine infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer, using PC control and OMNIC software in 0.1 mm NaCl cells. ^{31}P NMR spectra were recorded on a Varian 300-VXR spectrometer, operating at 121 MHz. The reported ^{31}P chemical shifts are referenced to external H_3PO_4 (85%), taken to have $\delta = 0$. ^{1}H and ^{13}C NMR spectra were

recorded on a Varian Gemini-200 spectrometer, operating at 200 and 50 MHz respectively. The C and H microanalyses were performed by Atlantic Microlab, Norcross, GA.

C. Preparation of Compounds

1. $OHCCCo_3(CO)_7$(bpcd) (2)

To 0.094 g (0.2 mmol) of $OHCCCo_3(CO)_9$ and 0.093 g (0.2 mmol) of bpcd in 20 mL of CH_2Cl_2 at 0 ^oC was added 0.02 g (0.27 mmol) of Me_3NO under argon flush. The reaction solution was stirred for 10 min at r.t., after which the solution was removed under vacuum. The crude product was purified by low-temperature (-78 ^oC) column chromatography over silica gel using CH_2Cl_2-petroleum ether (7:3) as the eluent. A black-green compound was obtained in 34% yield (60 mg). IR (CH_2Cl_2): ν(CO) 2071 (s), 2022 (s), 1753 (w, asymmetric bpcd C=O), 1718 (m, symmetric bpcd C=O) cm^{-1}. $^{31}P\{^1H\}$ NMR (THF, r.t.): δ 43 (m). $^{31}P\{^1H\}$ NMR (THF, -86 ^oC): δ 64 (chelate), 41 (bridge), 37 (bridge). ^1H NMR (CD_2Cl_2, r.t.): δ 3.28 (s, bpcd-H, 2H), 7.25-7.42 (m, Ph-H, 20H), 10.43 (s, CHO, 1H). Anal. Calcd (found) for $C_{38}H_{23}Co_3O_{10}P_2$: C 52.59 (52.62), H 2.60 (2.88).

2. $HCCo_3(CO)_7$(bpcd) (4)

To 0.221 g (0.5 mmol) of $HCCo_3(CO)_9$ and 0.232 g (0.5 mmol) of bpcd in 30 mL of CH_2Cl_2 at room temperature was added 0.075 g (1.0 mmol) of Me_3NO under argon

flush. The color of the solution changed from purple to black immediately. The reaction, which was monitored by TLC, was complete in 10 min. The reaction solution was removed under vacuum. The crude product was purified by low-temperature (-78 ^{o}C) column chromatography over silica gel using CH_2Cl_2 as the eluent. A black product was obtained in 23% yield (100 mg). IR (CH_2Cl_2): ν(CO) 2063 (s), 2008 (s), 1748 (w, asymmetric bpcd C=O), 1717 (m, symmetric bpcd C=O) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (THF, r.t.): δ 51 (m). $^{31}P\{^{1}H\}$ NMR (THF, -86 ^{o}C): δ 65 (chelate), 41 (bridge). ^{1}H NMR (CD_2Cl_2, r.t.): δ 3.29 (s, bpcd-H), 7.35-7.49 (m, Ph-H), 10.99 (s, CH). The $HCCo_3(CO)_7$(bpcd) was not submitted for combustion analysis because of its instability.

3. P-C bond cleavage compound (5)

To 0.1 g (0.1 mmol) of $OHCCCo_3(CO)_7$(bpcd) in a Schlenk tube was added 20 mL of toluene. After the vessel was sealed, the vessel was heated to 60 ^{o}C for 3 hr. The solution was allowed to cool and then examined by IR and TLC analyses, which revealed the consumption of the starting materials and the presence of the desired product. Cluster **5** was isolated by chromatography over silica gel using CH_2Cl_2 as the eluting solvent. A green product was obtained in 39% yield (30 mg). IR (CH_2Cl_2): ν(CO) 2072 (s), 2028 (s), 1711 (w, asymmetric bpcd C=O), 1686 (m, symmetric bpcd C=O) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (toluene, r.t.): δ 20 (m), 171 (m). $^{31}P\{^{1}H\}$ NMR (toluene, -86 ^{o}C): δ 23 (s), 173 (s). Anal. Calcd (found) for $C_{30}H_{17}Co_3O_9P_2$ (1/5 · C_6H_{14}): C 48.18 (48.29), H 2.57 (2.45).

D. X-ray Crystallography

A dark black-green crystal of $OHCCCo_3(CO)_7$(bpcd) (2) was grown from a CH_2Cl_2 solution that had been layered with heptane; a black crystal of $HCCo_3(CO)_7$(bpcd) (4) was grown from a CH_2Cl_2 solution that had been layered with heptane; a dark green crystal of cluster **5** was grown from a CH_2Cl_2 solution that had been layered with heptane. All X-ray data were collected on a Rigaku AFC-6S diffractometer using the θ-2θ mode at a fixed scan rate with multiple scans for weak reflections. The structure was solved by using SIR92,[5] and refined and analyzed using TEXSAN[6] and PLATON.[7] Crystal, intensity measurement and refinement data are given in Table 2.1.

Table 2.1 X-ray crystallographic data and processing parameters for clusters **2**, **4**, and **5**

		2	**4**	**5**
Space group		Monoclinic ($P2_1/c$)	Triclinic (P-1)	Monoclinic (Cc)
Cell constants	a, Å	8.854(2)	11.5588(9)	10.3947(12)
	b, Å	19.468(5)	12.4927(10)	33.223(4)
	c, Å	20.867(5)	12.7968(10)	9.2043(10)
	a, deg	90	98.2680(10)	90
	ß, deg	92.895(4)	100.9140(10)	108.501(2)
	?, deg	90	101.2280(10)	90
	V, $Å^3$	3592.6(15)	1748.1(2)	3014.3(6)
Mol formula		$C_{38}H_{23}Co_3O_{10}P_2$	$C_{37}H_{23}Co_3O_9P_2$	$C_{30}H_{17}Co_3O_9P_2$
Fw		878.29	850.28	760.17
Formula units per cell (Z)		4	2	4
?, Mg /m^3		1.624	1.615	1.675
abs coeff (μ), mm^{-1}		1.517	1.554	1.791
? (Mo Kα), Å		0.71073	0.71073	0.71073
Collection range, deg		1.43 to 23.27	1.65 to 28.94	2.16 to 29.04
Total No. of data collected		15498	11012	9580
No. of independent data, I>3s(I)		5163	7730	4924
R		0.0356	0.0302	0.0486
R_W		0.0496	0.0372	0.0527

Chapter References

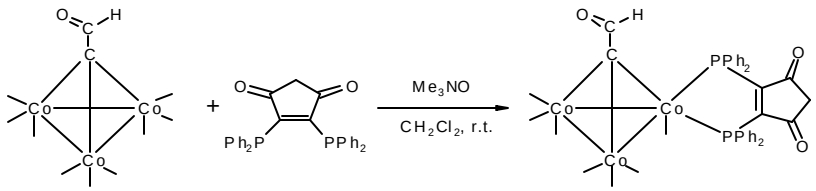
1. Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, 16, 758.
2. Nestle, M. O.; Hallgren, J. E.; Seyferth, D. *Inorg. Synth.* **1980**, 20, 226.
3. (a) Fenske, D.; Becher, H. J. *Chem. Ber.* **1974**, 107, 117. (b) Fenske, D. *Chem. Ber.* **1979**, 112, 363.
4. Kofen, W. G.; Backlawski, L. M. *J. Org. Chem.* **1976**, 41, 1879.
5. Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, 26, 343.
6. **TEXSAN-TEXRAY** *Structure Analysis Package;* Molecular Structure Corporation, Vers. 1.7-1, March **1995**.
7. Spek, A. L. *Acta Crystallogr.* **1982**, 29, 203.

Chapter III Results

A. Synthesis and Spectroscopic Properties of $OHCCCo_3(CO)_7(bpcd)$ (2)

Due to the difficulty in preparing the diphosphine-substituted clusters $RCCo_3(CO)_7(bpcd)$ (R=CHO, H) by the thermolysis route,[1] we examined the reaction between $RCCo_3(CO)_9$ (R=H, CHO) and bpcd in the presence of the oxidative-decarbonylation reagent Me_3NO. It is known that this particular reagent offers the possibility of affording thermally sensitive organometallic compounds under mild conditions.[2]

Treatment of an equimolar mixture of $OHCCCo_3(CO)_9$ and bpcd with a slight excess of Me_3NO in CH_2Cl_2 at room temperature led to an immediate reaction (Eq. 3.1), as judged by the immediate color change of the reaction solution from purple to black. IR and TLC analyses also showed a new compound. $OHCCCo_3(CO)_7(bpcd)$ was isolated by column chromatography over silica gel at –78 ^oC using CH_2Cl_2/petroleum ether (1:1). $OHCCCo_3(CO)_7(bpcd)$ is soluble in polar solvents and it appears to be air-sensitive in both the solid state and in solution; it is stable under a CO atmosphere for an extended period of time.



1 2

Eq. 3.1

The IR spectrum of $OHCCCo_3(CO)_7(bpcd)$ reveals terminal carbonyl stretching bands at 2071 (s), 2022 (vs) cm^{-1}. The ancillary bpcd ligand exhibits ν(CO) bands belonging to the dione moiety at 1753 and 1718 cm^{-1} typical of a cluster coordinated bpcd ligand.[3]

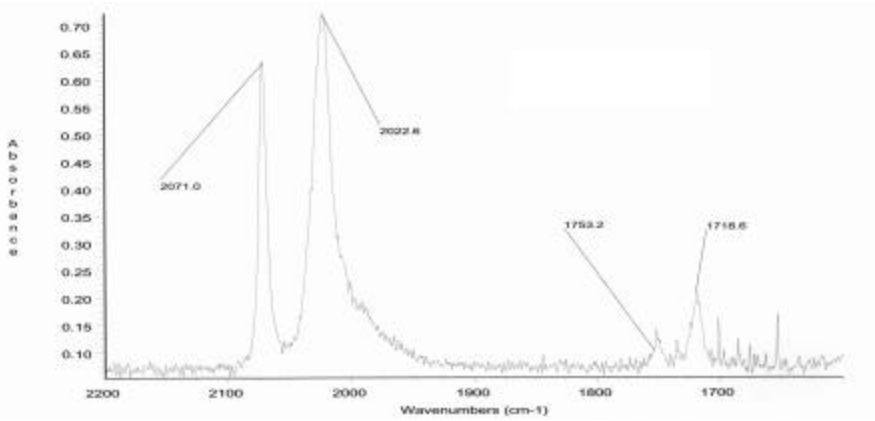
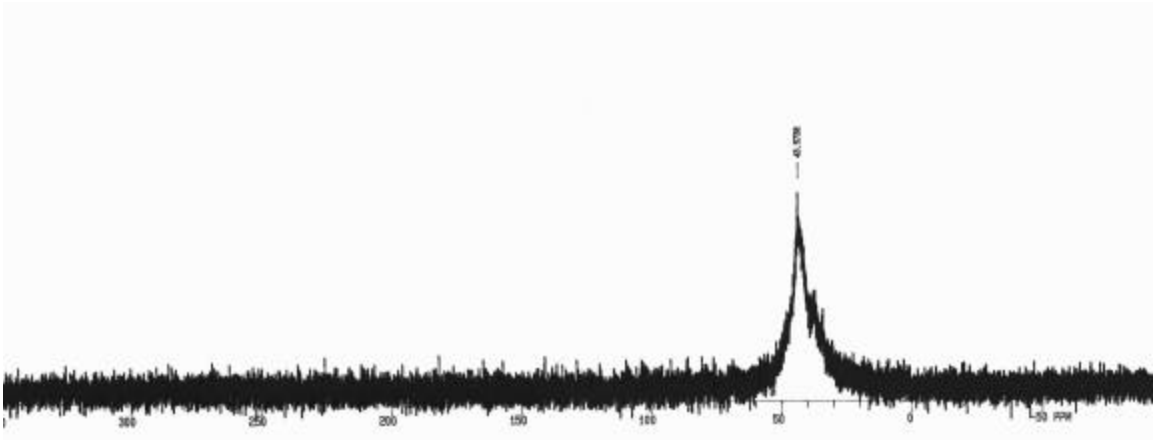


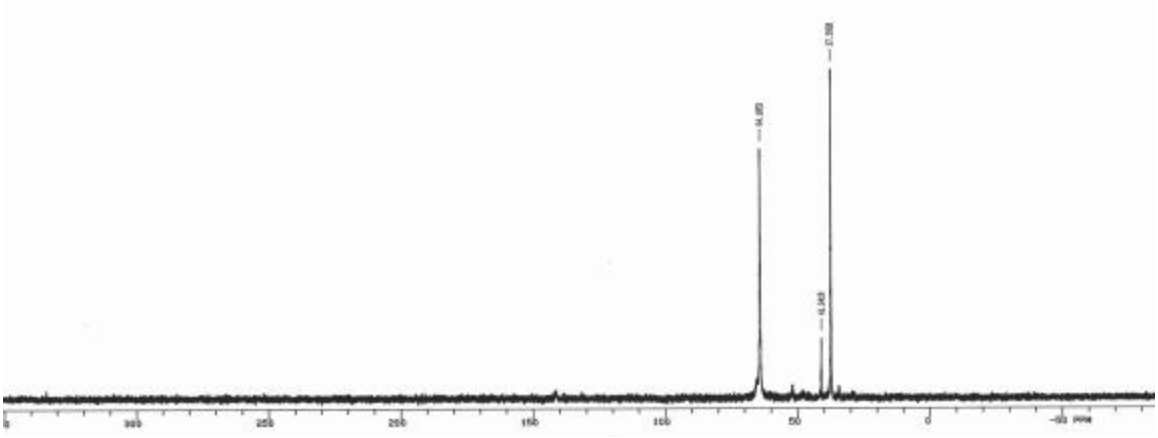
Figure 3.1 IR Spectrum of $OHCCCo_3(CO)_7(bpcd)$ **(2)** recorded in CH_2Cl_2

The $^{31}P\{^1H\}$ NMR spectrum of $OHCCCo_3(CO)_7(bpcd)$ in THF at room temperature exhibits a single, broad resonance at ca. δ 43, whose relative location is strongly suggestive of a bridging bpcd ligand. Given that the cluster $OHCCCo_3(CO)_7(bpcd)$ exhibited temperature-dependent ^{31}P spectra due to equilibrating chelating and bridging bpcd isomers, we investigated the VT ^{31}P NMR behavior of **2**. Cooling a sample of $OHCCCo_3(CO)_7(bpcd)$ down to 187 K leads to the appearance of three distinct ^{31}P resonances at δ 64.2, 41.0 and 37.4. Samples of $OHCCCo_3(CO)_7(bpcd)$ that were cycled over the temperature range of 187 K to 298 K afforded unchanged spectral data, suggesting that the observed VT behavior was the result of a ligand

equilibration about the cluster polyhedron. On the basis of the bpcd chemical shift and symmetry considerations, we are able to assign the ^{31}P NMR data to three specific bpcd isomers of **2**, as shown below.



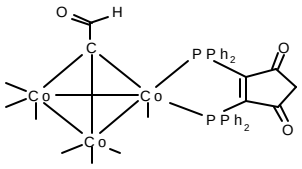
(a)



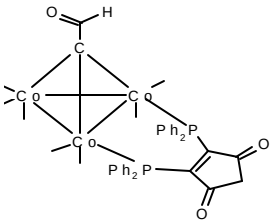
(b)

Figure 3.2 ^{31}P NMR spectra of $OHCCCo_3(CO)_7(bpcd)$ **(2)** recorded in THF

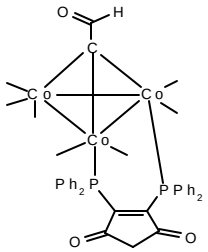
(a) room temperature, (b) 187 K



64.1 ppm
equivalent PPh_2 groups



37.4 ppm
equivalent PPh_2 groups



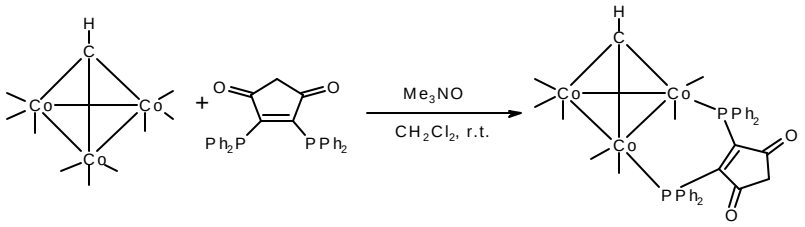
41.0 ppm
equivalent PPh_2 groups

Scheme 3.1

The high-field resonances at δ 37.4 and 41.0 are readily assigned to the bridging isomer of $OHCCCo_3(CO)_7$(bpcd) since bridging diphosphine ligands are known to experience a greater nuclear shielding relative to the same ligand in a chelating mode.[4] Moreover, the two resonances associated with this isomer indicate that there are two non-identical phosphines present in this isomer. They are not in the equal amount and the species at δ 41.0 contributes only 10%. It is our assumption that minor bridging isomer (10%) has the bpcd ligand residing in the axial position at each of the two cobalt atoms. The major bridging bpcd isomer has the bpcd ligand in the equatorial plane. The two bridging isomers contribute 50% to the total bridging isomer composition at 187 K; the remaining species present in solution is assigned to the chelating bpcd isomer based on its higher-field chemical shift. As a rule of thumb, chelating ligands of this nature typically appear from δ 50-75. The single resonance peak at δ 64.1 is consistent with the X-ray structure of $OHCCCo_3(CO)_7$(bpcd), which possesses two identical chelating phosphine groups that reside in the equatorial plane defined by the cobalt atoms.

B. Synthesis and Spectroscopic Properties of $HCCo_3(CO)_7$(bpcd) (4)

As in the cluster $OHCCCo_3(CO)_7$(bpcd), the cluster $HCCo_3(CO)_7$(bpcd) was synthesized by using Me_3NO at ambient conditions. A clean reaction was observed between $HCCo_3(CO)_9$ and bpcd. A black product was obtained by column chromatography over silica gel at –78 ^oC using CH_2Cl_2/petroleum ether (1:1); the isolated compound is very air sensitive and temperature sensitive.



3 4 Eq. 3.2

The IR spectrum of $HCCo_3(CO)_7$(bpcd) reveals terminal carbonyl stretching bands at 2063 (s), 2008 (vs) cm^{-1}. The ancillary bpcd ligand exhibits ν(CO) bands belonging to the dione moiety at 1748 (w) and 1717 (m) cm^{-1} typical of a cluster coordinated bpcd ligand.

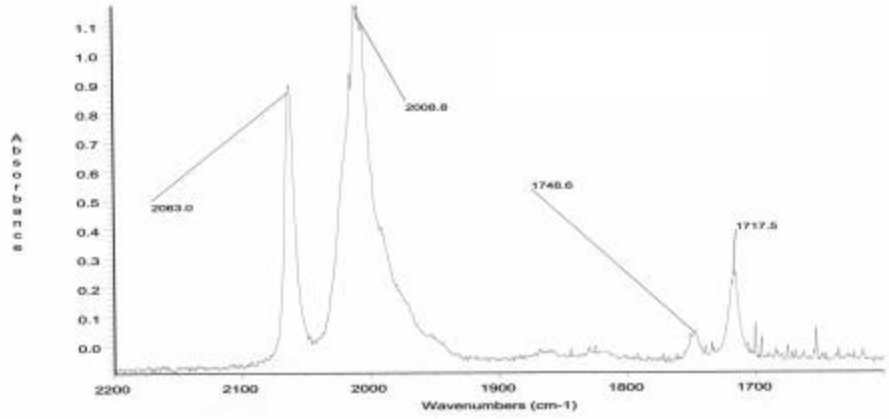
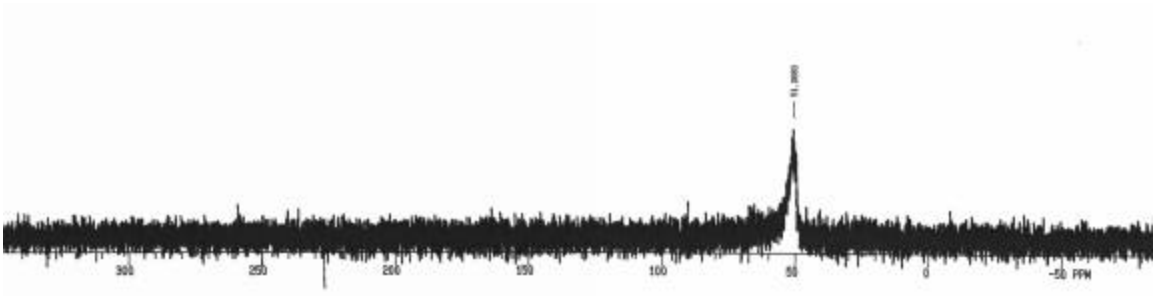


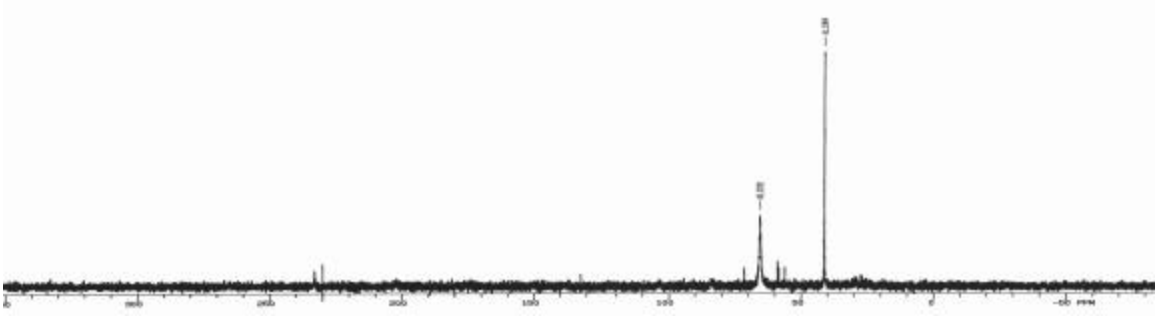
Figure 3.3 IR spectrum of $HCCo_3(CO)_7$(bpcd) **(4)** recorded in CH_2Cl_2

The $^{31}P\{^{1}H\}$ NMR spectrum of $HCCo_3(CO)_7$(bpcd) in THF at room temperature exhibits a single, broad resonance at ca. δ 51.0, whose relative location is suggestive of a chelating bpcd ligand. The cluster $HCCo_3(CO)_7$(bpcd) exhibited temperature-dependent ^{31}P spectra due to equilibrating chelating and bridging bpcd isomers. We investigated the VT ^{31}P NMR behavior of **4** and found that cooling a sample of $HCCo_3(CO)_7$(bpcd) down to 187 K leads to the appearance of two distinct ^{31}P resonances at δ 65.6 and 41.2. Samples of $HCCo_3(CO)_7$(bpcd) that were cycled over the temperature range of 187 K to 298 K afforded unchanged spectral data, suggesting that the observed VT behavior was the result of a ligand equilibration about the cluster polyhedron. On the basis of the bpcd chemical shift and symmetry considerations, we are able to assign the ^{31}P NMR data to two specific bpcd isomers of **4**, as shown below.

The high-field resonance at δ 41.2 is readily assigned to the bridging isomer of $HCCo_3(CO)_7$(bpcd) since bridging diphosphine ligands are known to experience a greater nuclear shielding relative to the same ligand in a chelating mode. Moreover, the single resonance associated with this isomer indicates that the bpcd ligand resides in the equatorial plane defined by the cobalt atoms, which is consistent with the X-ray structure of $HCCo_3(CO)_7$(bpcd). This bridged isomer contributes 42% to the isomer composition at 187 K. The remaining species present in solution is assigned to the chelating bpcd isomer based on its higher field chemical shift δ 65.6.



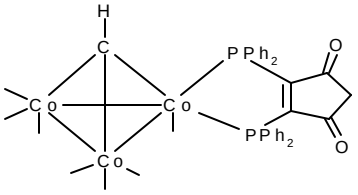
(a)



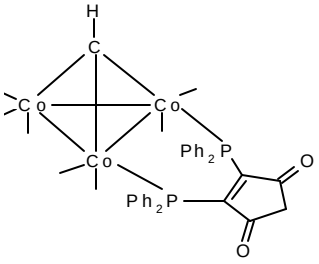
(b)

Figure 3.4 ^{31}P NMR spectra of $HCCo_3(CO)_7(bpcd)$ **(4)** recorded in THF

(a) room temperature, (b) 187 K



65.6 ppm
equivalent PPh_2 groups

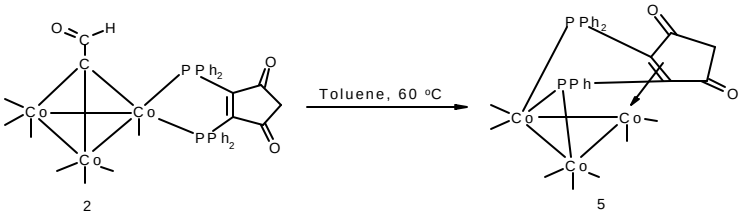


41.2 ppm
equivalent PPh_2 groups

Scheme 3.2

C. Synthesis and Spectroscopic Properties of the P-C Bond Cleavage Compound (5)

The cluster $OHCCCo_3(CO)_7(bpcd)$ readily loses CO and transforms to cluster **5** upon gentle heating in toluene. The thermolysis reaction unequivocally establishes the intermediacy of the diphosphine cluster **2** in the formation of **5** and allows the overall reaction to be delineated as illustrated in equation 3.3. The inability to prepare cluster **2** in the thermolysis reactions involving $OHCCCo_3(CO)_9$ and bpcd provides an important view on the relative rates of formation for clusters **2** and **5**. Starting from cluster $OHCCCo_3(CO)_9$, the observation of cluster **2** is not expected if the subsequent reactions leading to **5** all occur at faster rates. Thermolysis of $HCCo_3(CO)_7(bpcd)$ also afforded cluster **5** in very low yield.



2 5 Eq. 3.3

Cluster **5** was isolated by chromatography over silica gel using CH_2Cl_2 and characterized spectroscopically in solution. The IR spectrum of **5** display terminal carbonyl stretching bands at 2072 (s) and 2028 (vs) cm^{-1} along with the characteristic bpcd carbonyl bands at 1711 (w) and 1686 (w) cm^{-1}. As with the precursor cluster 2, these latter two bands are assigned to the asymmetric and symmetric ν(C=O) modes of the bpcd dione ligand.

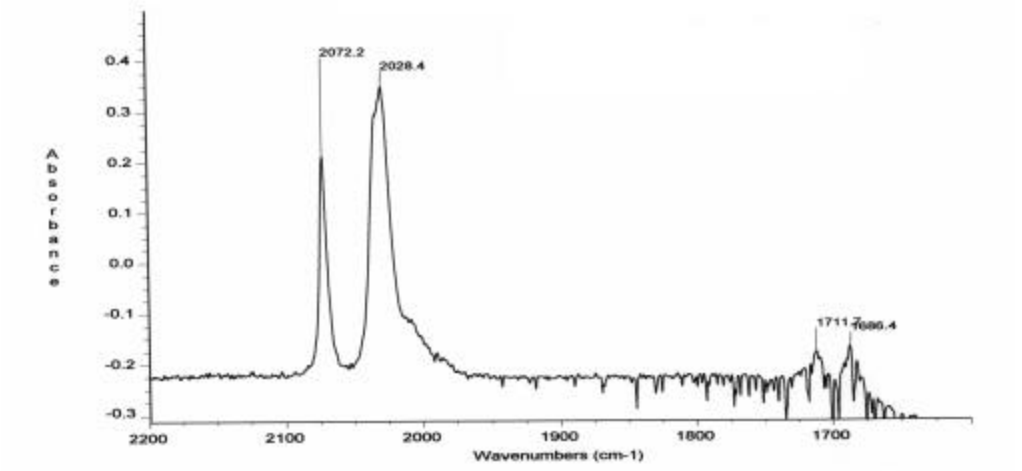
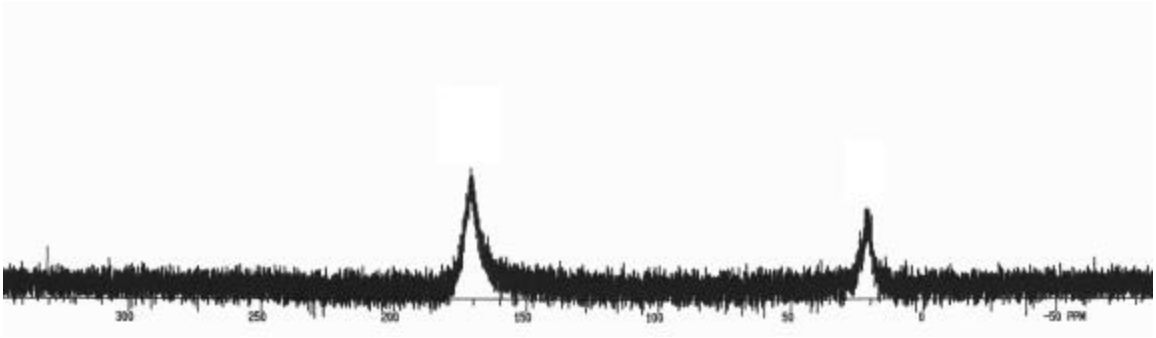
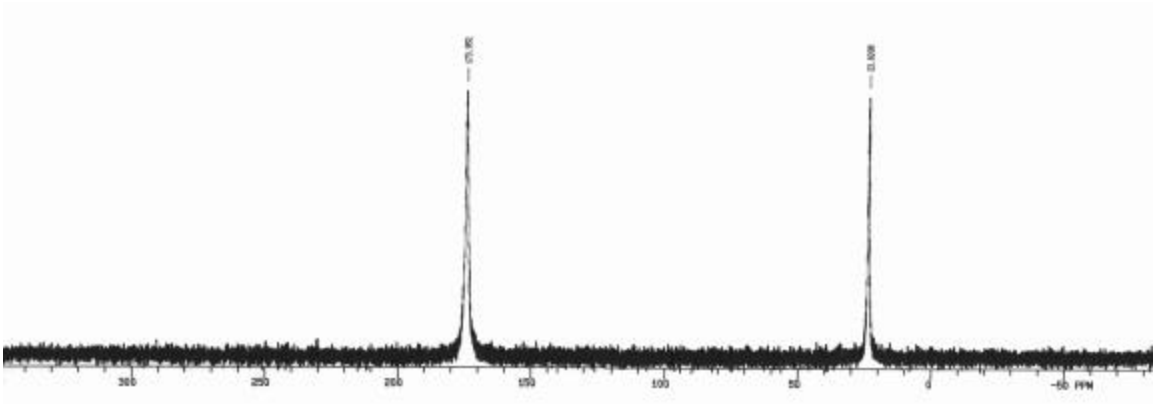


Figure 3.5 IR spectrum of the P-C bond cleavage compound **(5)** recorded in CH_2Cl_2

Two broad resonances at δ 171.1 and 20.8 in the $^{31}P\{^1H\}$ NMR spectrum were observed for cluster **5** in toluene at room temperature. The same sample was next examined at 187 K in order to reduce the scalar coupling between the ^{31}P and ^{59}Co nuclei. Reduced temperatures effectively serve to shorten the molecular correlation time (τ_c) and have been shown to afford sharp ^{31}P resonances in other phosphine-substituted cobalt clusters.[5] The low-temperature $^{31}P\{^1H\}$ NMR spectrum of **5** revealed the same ^{31}P resonances that were observed at room temperature only sharper, which is consistent with the X-ray structure that shows two different phosphine moieties. Based on the bpcd chemical shift and symmetry considerations, these two resonances at d 171.1 and 20.8 can be assigned to the μ_2-phosphido and the PPh_2 moieties respectively, as shown below.

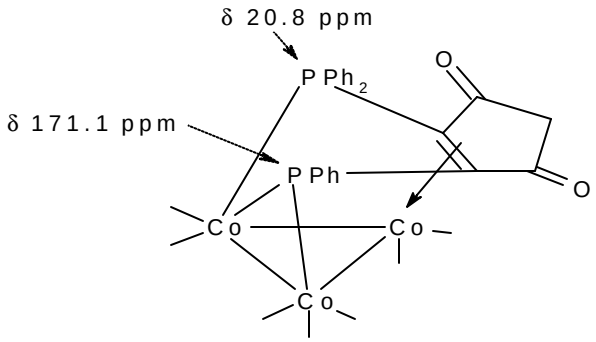


(a)



(b)

Figure 3.6 ^{31}P NMR spectra of the P-C bond cleavage compound **(5)** recorded in toluene, (a) room temperature, (b) 187 K



Scheme 3.3

D. X-ray Diffraction Structure of $OHCCCo_3(CO)_7(bpcd)$ (2)

Single crystals of $OHCCCo_3(CO)_7(bpcd)$ were grown from a CH_2Cl_2 solution containing $OHCCCo_3(CO)_7(bpcd)$ that had been layered with heptane. The X-ray data collection and processing parameters for **2** was given in Table 2.1, with the selected bond distances and angles given in Table 3.1 and Table 3.2. The ORTEP diagram is shown in Figure 3.7.

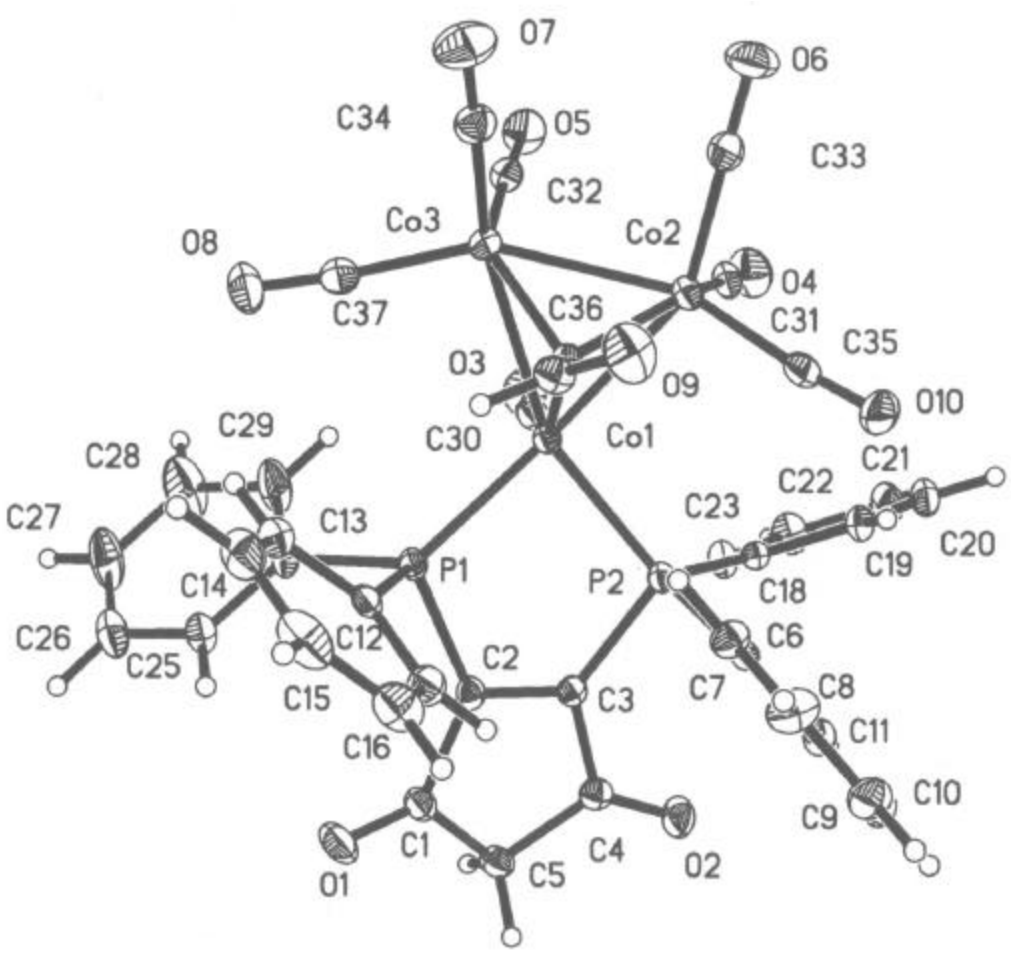


Figure 3.7 The ORTEP diagram of $OHCCCo_3(CO)_7(bpcd)$ **(2)**

Table 3.1 Positional parameters for the non-hydrogen atoms in $OHCCCo_3(CO)_7(bpcd)$ **(2)** with estimated standard deviations in parentheses

atom	x ($x10^4$)	y ($x10^4$)	z ($x10^4$)	B, ($Å^2 \times 10^3$)
Co(1)	342(1)	6221(1)	2394(1)	22(1)
Co(2)	2353(1)	5662(1)	3094(1)	29(1)
Co(3)	2001(1)	5326(1)	1943(1)	28(1)
P(1)	-553(1)	6918(1)	1623(1)	24(1)
P(2)	-460(1)	6944(1)	3114(1)	23(1)
O(1)	-2810(3)	8349(1)	1271(1)	52(1)
O(2)	-3513(3)	7972(1)	3447(1)	45(1)
O(3)	-2172(3)	5253(1)	2523(1)	48(1)
O(4)	112(3)	4850(1)	3790(1)	54(1)
O(5)	551(3)	4051(1)	2366(1)	49(1)
O(6)	5060(3)	4802(1)	3258(1)	58(1)
O(7)	5027(3)	4870(2)	1618(2)	68(1)
O(8)	913(4)	5454(2)	607(1)	75(1)
O(9)	4840(3)	6770(2)	2432(1)	56(1)
O(10)	3545(3)	6709(1)	3991(1)	52(1)
C(1)	-2852(4)	8065(2)	1779(2)	30(1)
C(2)	-1826(3)	7504(2)	2035(2)	25(1)
C(3)	-1930(3)	7440(2)	2669(2)	23(1)
C(4)	-3170(4)	7896(2)	2899(2)	28(1)
C(5)	-3869(4)	8252(2)	2314(2)	32(1)
C(6)	626(3)	7679(2)	3445(2)	24(1)
C(7)	1982(4)	7872(2)	3195(2)	33(1)
C(8)	2714(4)	8459(2)	3417(2)	45(1)
C(9)	2094(4)	8857(2)	3887(2)	43(1)

C(10)	761(4)	8668(2)	4137(2)	37(1)
C(11)	20(4)	8077(2)	3924(2)	31(1)
C(12)	798(3)	7480(2)	1244(2)	26(1)
C(13)	1501(4)	7260(2)	700(2)	36(1)
C(14)	2663(4)	7640(2)	457(2)	46(1)
C(15)	3117(4)	8240(2)	746(2)	53(1)
C(16)	2406(4)	8473(2)	1276(2)	47(1)
C(17)	1240(4)	8098(2)	1527(2)	35(1)
C(18)	-1283(3)	6567(2)	3819(2)	25(1)
C(19)	-386(4)	6507(2)	4386(2)	29(1)
C(20)	-902(4)	6170(2)	4908(2)	36(1)
C(21)	-2328(4)	5882(2)	4876(2)	42(1)
C(22)	-3227(4)	5941(2)	4323(2)	40(1)
C(23)	-2714(4)	6278(2)	3789(2)	32(1)
C(24)	-1820(4)	6636(2)	948(2)	31(1)
C(25)	-2240(4)	7090(2)	458(2)	35(1)
C(26)	-3268(4)	6901(2)	-28(2)	46(1)
C(27)	-3854(5)	6250(3)	-44(2)	65(1)
C(28)	-3454(6)	5797(3)	431(2)	82(2)
C(29)	-2438(5)	5988(2)	932(2)	57(1)
C(30)	-1229(4)	5649(2)	2471(2)	31(1)
C(31)	972(4)	5160(2)	3523(2)	38(1)
C(32)	1078(4)	4548(2)	2185(2)	35(1)
C(33)	4011(4)	5136(2)	3189(2)	38(1)
C(34)	3873(4)	5048(2)	1755(2)	39(1)
C(35)	3032(4)	6322(2)	3640(2)	35(1)
C(36)	2456(3)	6208(2)	2331(2)	25(1)
C(37)	1301(4)	5429(2)	1133(2)	44(1)
C(38)	3677(4)	6636(2)	2128(2)	34(1)

Table 3.2 Selected bond distances (Å) and angles (deg) for $OHCCCo_3(CO)_7$(bpcd) **(2)**

Bond distances			
Co(1)-C(30)	1.795(4)	Co(1)-C(36)	1.884(3)
Co(1)-P(2)	2.2024(10)	Co(1)-P(1)	2.2207(10)
Co(1)-Co(3)	2.4933(7)	Co(1)-Co(2)	2.4944(7)
Co(2)-C(33)	1.793(4)	Co(2)-C(35)	1.801(4)
Co(2)-C(31)	1.834(4)	Co(2)-C(36)	1.921(3)
Co(2)-Co(3)	2.4923(8)	Co(3)-C(37)	1.783(4)
Co(3)-C(32)	1.805(4)	Co(3)-C(34)	1.805(4)
Co(3)-C(36)	1.933(3)	P(1)-C(12)	1.831(3)
P(1)-C(24)	1.841(3)	P(1)-C(2)	1.845(3)
P(2)-C(18)	1.828(3)	P(2)-C(3)	1.836(3)
P(2)-C(6)	1.840(3)	O(1)-C(1)	1.197(4)
O(2)-C(4)	1.206(4)	O(3)-C(30)	1.145(4)
O(4)-C(31)	1.139(4)	O(5)-C(32)	1.145(4)
O(6)-C(33)	1.137(4)	O(7)-C(34)	1.131(4)
O(8)-C(37)	1.134(4)	O(9)-C(38)	1.210(4)
O(10)-C(35)	1.131(4)	C(5)-C(4)	1.509(4)
C(5)-C(1)	1.513(4)	C(1)-C(2)	1.502(4)
C(2)-C(3)	1.336(4)	C(3)-C(4)	1.509(4)
C(6)-C(7)	1.385(4)	C(6)-C(11)	1.394(4)
C(7)-C(8)	1.381(5)	C(8)-C(9)	1.387(5)
C(9)-C(10)	1.364(5)	C(10)-C(11)	1.387(5)
C(12)-C(17)	1.387(5)	C(12)-C(13)	1.389(4)
C(13)-C(14)	1.384(5)	C(15)-C(14)	1.365(6)
C(15)-C(16)	1.376(5)	C(16)-C(17)	1.389(5)
C(18)-C(23)	1.386(4)	C(18)-C(19)	1.397(4)
C(19)-C(20)	1.370(4)	C(20)-C(21)	1.381(5)
C(21)-C(22)	1.373(5)	C(22)-C(23)	1.389(5)
C(24)-C(29)	1.375(5)	C(24)-C(25)	1.388(5)
C(25)-C(26)	1.378(5)	C(26)-C(27)	1.370(6)
C(27)-C(28)	1.359(6)	C(29)-C(28)	1.395(5)
C(36)-C(38)	1.445(4)		

Bond angles			
C(30)-Co(1)-C(36)	140.88(14)	C(30)-Co(1)-P(2)	93.31(11)
C(36)-Co(1)-P(2)	114.31(10)	C(30)-Co(1)-P(1)	101.19(11)
C(36)-Co(1)-P(1)	106.06	P(2)-Co(1)-P(1)	89.28(4)
C(30)-Co(1)-Co(3)	94.25(11)	C(36)-Co(1)-Co(3)	50.07(10)
P(2)-Co(1)-Co(3)	156.96(3)	P(1)-Co(1)-Co(3)	110.47(3)
C(30)-Co(1)-Co(2)	102.17(10)	C(36)-Co(1)-Co(2)	49.67(10)
P(2)-Co(1)-Co(2)	97.16(3)	P(1)-Co(1)-Co(2)	155.33(3)
Co(1)-Co(2)-Co(3)	59.96(2)	C(33)-Co(2)-C(35)	95.27(15)
C(33)-Co(2)-C(31)	101.78(16)	C(35)-Co(2)-C(31)	106.29(16)
C(33)-Co(2)-C(36)	109.55(15)	C(35)-Co(2)-C(36)	95.78(15)
C(31)-Co(2)-C(36)	139.58(14)	C(33)-Co(2)-Co(3)	91.04(11)
C(35)-Co(2)-Co(3)	144.92(12)	C(31)-Co(2)-Co(3)	106.09(11)
C(36)-Co(2)-Co(3)	49.92(9)	C(33)-Co(2)-Co(1)	150.46(12)
C(35)-Co(2)-Co(1)	105.38(11)	C(31)-Co(2)-Co(1)	92.58(11)
C(36)-Co(2)-Co(1)	48.39(9)	Co(3)-Co(2)-Co(1)	60.000(19)
C(37)-Co(3)-C(32)	102.67(16)	C(37)-Co(3)-C(34)	96.09(17)
C(32)-Co(3)-C(34)	104.11(16)	C(37)-Co(3)-C(36)	110.59(15)
C(32)-Co(3)-C(36)	135.79(15)	C(34)-Co(3)-C(36)	100.51(15)
C(37)-Co(3)-Co(2)	154.76(12)	C(32)-Co(3)-Co(2)	89.28(11)
C(34)-Co(3)-Co(2)	102.52(12)	C(36)-Co(3)-Co(2)	49.49(9)
C(37)-Co(3)-Co(1)	95.50(12)	C(32)-Co(3)-Co(1)	101.37(11)
C(34)-Co(3)-Co(1)	148.86(12)	C(36)-Co(3)-Co(1)	48.36(9)
Co(2)-Co(3)-Co(1)	60.042(18)	C(12)-P(1)-C(24)	103.49(15)
C(12)-P(1)-C(2)	105.06(14)	C(24)-P(1)-C(2)	100.28(14)
C(12)-P(1)-Co(1)	117.52(10)	C(24)-P(1)-Co(1)	123.59(12)
C(2)-P(1)-Co(1)	104.16(11)	C(18)-P(2)-C(3)	108.49(14)
C(18)-P(2)-C(6)	103.42(14)	C(3)-P(2)-C(6)	97.11(14)
C(18)-P(2)-Co(1)	116.63(11)	C(3)-P(2)-Co(1)	103.65(10)
C(6)-P(2)-Co(1)	124.97(11)	C(4)-C(5)-C(1)	104.5(3)

O(1)-C(1)-C(2)	127.3(3)	O(1)-C(1)-C(5)	126.0(3)
C(2)-C(1)-C(5)	106.5(3)	C(3)-C(2)-C(1)	110.4(3)
C(3)-C(2)-P(1)	118.6(2)	C(1)-C(2)-P(1)	131.0(2)
C(2)-C(3)-C(4)	110.4(3)	C(2)-C(3)-P(2)	117.8(2)
C(4)-C(3)-P(2)	131.1(2)	O(2)-C(4)-C(5)	126.8(3)
O(2)-C(4)-C(3)	126.5(3)	C(5)-C(4)-C(3)	106.7(3)
C(7)-C(6)-C(11)	119.5(3)	C(7)-C(6)-P(2)	121.1(2)
C(11)-C(6)-P(2)	119.2(2)	C(8)-C(7)-C(6)	120.0(3)
C(7)-C(8)-C(9)	120.2(3)	C(10)-C(9)-C(8)	120.0(3)
C(9)-C(10)-C(11)	120.5(3)	C(10)-C(11)-C(6)	119.8(3)
C(17)-C(12)-C(13)	119.1(3)	C(17)-C(12)-P(1)	120.7(3)
C(13)-C(12)-P(1)	119.9(3)	C(14)-C(13)-C(12)	120.4(4)
C(14)-C(15)-C(16)	120.0(4)	C(15)-C(16)-C(17)	120.6(4)
C(12)-C(17)-C(16)	119.6(3)	C(23)-C(18)-C(19)	118.9(3)
C(23)-C(18)-P(2)	121.9(2)	C(19)-C(18)-P(2)	118.9(2)
C(20)-C(19)-C(18)	121.1(3)	C(19)-C(20)-C(21)	119.8(3)
C(22)-C(21)-C(20)	119.8(3)	C(21)-C(22)-C(23)	121.0(3)
C(18)-C(23)-C(22)	119.4(3)	C(29)-C(24)-C(25)	118.4(3)
C(29)-C(24)-P(1)	121.2(3)	C(25)-C(24)-P(1)	120.2(3)
C(26)-C(25)-C(24)	120.9(3)	C(27)-C(26)-C(25)	120.0(4)
C(28)-C(27)-C(26)	119.9(4)	C(24)-C(29)-C(28)	120.1(4)
C(27)-C(28)-C(29)	120.6(4)	O(3)-C(30)-Co(1)	176.0(3)
O(4)-C(31)-Co(2)	179.8(4)	O(5)-C(32)-Co(3)	176.2(3)
O(6)-C(33)-Co(2)	179.0(4)	O(7)-C(34)-Co(3)	177.8(4)
O(10)-C(35)-Co(2)	175.3(3)	C(38)-C(36)-Co(1)	140.8(2)
C(38)-C(36)-Co(2)	129.1(2)	Co(1)-C(36)-Co(2)	81.94(12)
C(38)-C(36)-Co(3)	122.2(2)	Co(1)-C(36)-Co(3)	81.57(12)
Co(2)-C(36)-Co(3)	80.59(13)	C(15)-C(14)-C(13)	120.2(4)
O(8)-C(37)-Co(3)	175.1(4)	O(9)-C(38)-C(36)	126.9(3)

E. X-ray Diffraction Structure of $HCCo_3(CO)_7(bpcd)$ (4)

Single crystals of $HCCo_3(CO)_7(bpcd)$ were grown from a CH_2Cl_2 solution containing $HCCo_3(CO)_7(bpcd)$ that had been layered with heptane. The X-ray data collection and processing parameters for **4** was given in Table 2.1, with the selected bond distances and angles given in Table 3.3 and Table 3.4. The ORTEP diagram is shown in Figure 3.8.

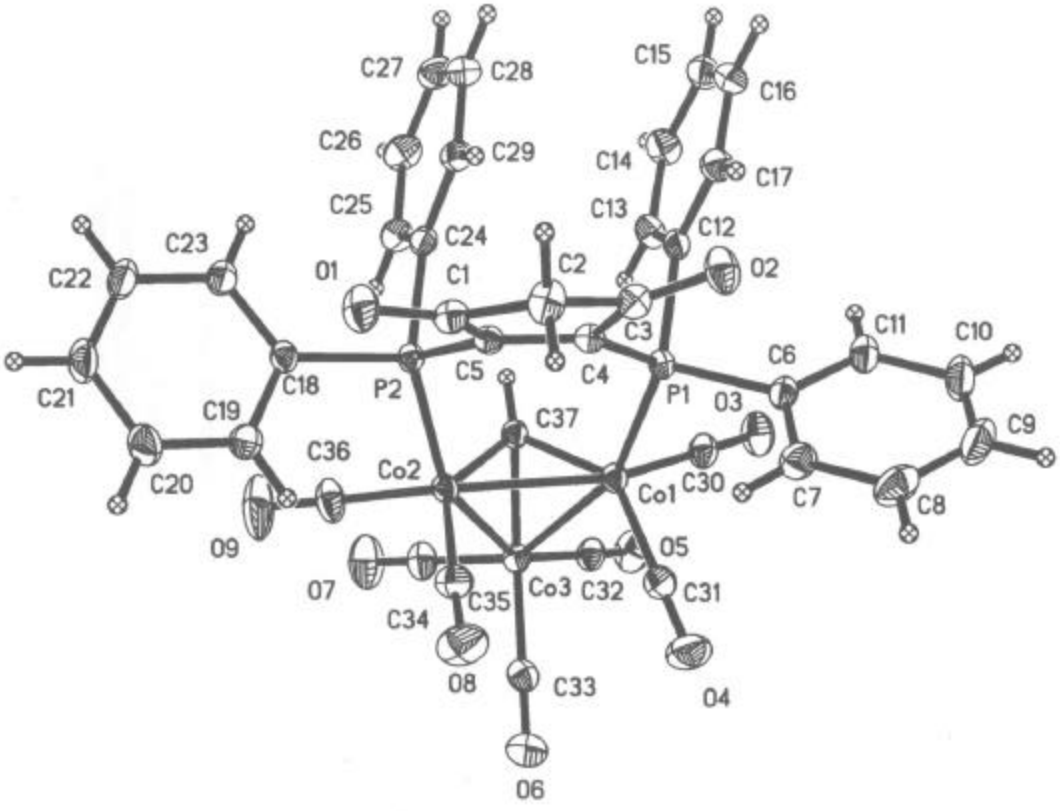


Figure 3.8 The ORTEP diagram of $HCCo_3(CO)_7(bpcd)$ **(4)**

Table 3.3 Positional parameters for the non-hydrogen atoms in $HCCo_3(CO)_7(bpcd)$ **(4)** with estimated standard deviations in parentheses

atom	x ($x10^4$)	y ($x10^4$)	z ($x10^4$)	B, ($Å^2 \times 10^3$)
Co(1)	3495(1)	2336(1)	2234(1)	27(1)
Co(2)	3122(1)	1844(1)	3963(1)	27(1)
Co(3)	4120(1)	684(1)	2842(1)	29(1)
P(1)	2352(1)	3532(1)	1939(1)	25(1)
P(2)	1535(1)	2498(1)	4156(1)	25(1)
O(1)	1203(2)	4806(1)	5626(1)	45(1)
O(2)	1741(2)	6020(1)	2440(1)	47(1)
O(3)	3293(2)	1629(2)	-77(1)	55(1)
O(4)	5880(2)	3906(2)	2942(2)	67(1)
O(5)	4337(2)	-481(2)	761(2)	60(1)
O(6)	6611(2)	1805(1)	4060(1)	50(1)
O(7)	3607(2)	-1391(2)	3656(2)	75(1)
O(8)	5130(2)	3650(2)	5251(2)	71(1)
O(9)	2719(3)	287(2)	5417(2)	92(1)
C(1)	1496(2)	4881(2)	4781(2)	31(1)
C(2)	1690(2)	5914(2)	4306(2)	40(1)
C(3)	1819(2)	5518(2)	3175(2)	32(1)
C(4)	1970(2)	4331(2)	3104(2)	27(1)
C(5)	1706(2)	3946(2)	3990(2)	26(1)
C(6)	3113(2)	4627(2)	1329(2)	31(1)
C(7)	4003(2)	5513(2)	1975(2)	43(1)
C(8)	4578(2)	6339(2)	1513(3)	57(1)
C(9)	4295(3)	6272(2)	403(3)	61(1)
C(10)	3456(3)	5385(2)	-245(2)	55(1)

C(11)	2851(2)	4562(2)	214(2)	39(1)
C(12)	874(2)	3013(2)	1000(2)	29(1)
C(13)	469(2)	1880(2)	575(2)	35(1)
C(14)	-636(2)	1479(2)	-169(2)	44(1)
C(15)	-1329(2)	2200(2)	-495(2)	45(1)
C(16)	-942(2)	3319(2)	-70(2)	44(1)
C(17)	145(2)	3727(2)	676(2)	36(1)
C(18)	1227(2)	2488(2)	5507(2)	30(1)
C(19)	2179(2)	2921(2)	6413(2)	41(1)
C(20)	1981(2)	2937(2)	7448(2)	50(1)
C(21)	831(2)	2527(2)	7590(2)	50(1)
C(22)	-106(2)	2069(2)	6706(2)	44(1)
C(23)	86(2)	2041(2)	5662(2)	35(1)
C(24)	63(2)	1875(2)	3253(2)	28(1)
C(25)	-280(2)	721(2)	2945(2)	36(1)
C(26)	-1407(2)	217(2)	2281(2)	47(1)
C(27)	-2192(2)	841(2)	1899(2)	48(1)
C(28)	-1872(2)	1981(2)	2204(2)	44(1)
C(29)	-761(2)	2500(2)	2884(2)	35(1)
C(30)	3379(2)	1910(2)	830(2)	36(1)
C(31)	4948(2)	3322(2)	2673(2)	40(1)
C(32)	4269(2)	3(2)	1562(2)	37(1)
C(33)	5664(2)	1358(2)	3584(2)	36(1)
C(34)	3808(2)	-570(2)	3365(2)	44(1)
C(35)	4340(2)	2948(2)	4765(2)	42(1)
C(36)	2882(3)	892(2)	4846(2)	50(1)
C(37)	2567(2)	1046(2)	2540(2)	29(1)

Table 3.4 Selected bond distances (Å) and angles (deg) for $HCCo_3(CO)_7(bpcd)$ **(4)**

Bond distances			
Co(1)-C(30)	1.770(2)	Co(1)-C(31)	1.814(2)
Co(1)-C(37)	1.8896(19)	Co(1)-P(1)	2.2052(5)
Co(1)-Co(2)	2.4720(4)	Co(1)-Co(3)	2.4937(4)
Co(2)-C(36)	1.773(2)	Co(2)-C(35)	1.797(2)
Co(2)-C(37)	1.8736(19)	Co(2)-P(2)	2.1888(5)
Co(2)-Co(3)	2.4837(4)	Co(3)-C(32)	1.789(2)
Co(3)-C(34)	1.791(2)	Co(3)-C(33)	1.827(2)
Co(3)-C(37)	1.9182(19)	P(1)-C(12)	1.830(2)
P(1)-C(6)	1.8309(19)	P(1)-C(4)	1.8445(19)
P(2)-C(24)	1.821(2)	P(2)-C(5)	1.8288(18)
P(2)-C(18)	1.8311(19)	O(1)-C(1)	1.203(2)
O(2)-C(3)	1.203(2)	O(3)-C(30)	1.143(3)
O(4)-C(31)	1.137(3)	O(5)-C(32)	1.137(3)
O(6)-C(33)	1.137(3)	O(7)-C(34)	1.137(3)
O(8)-C(35)	1.142(3)	O(9)-C(36)	1.139(3)
C(1)-C(2)	1.501(3)	C(1)-C(5)	1.520(2)
C(2)-C(3)	1.505(3)	C(3)-C(4)	1.518(3)
C(4)-C(5)	1.357(3)	C(6)-C(11)	1.388(3)
C(6)-C(7)	1.393(3)	C(7)-C(8)	1.383(3)
C(8)-C(9)	1.382(4)	C(9)-C(10)	1.367(4)
C(10)-C(11)	1.393(3)	C(12)-C(13)	1.394(3)
C(12)-C(17)	1.394(3)	C(13)-C(14)	1.393(3)
C(14)-C(15)	1.374(3)	C(15)-C(16)	1.377(3)
C(16)-C(17)	1.381(3)	C(18)-C(23)	1.391(3)
C(18)-C(19)	1.398(3)	C(19)-C(20)	1.383(3)
C(20)-C(21)	1.384(4)	C(21)-C(22)	1.375(4)
C(22)-C(23)	1.391(3)	C(24)-C(25)	1.395(3)
C(24)-C(29)	1.402(3)	C(25)-C(26)	1.386(3)
C(26)-C(27)	1.374(4)	C(27)-C(28)	1.378(3)
C(28)-C(29)	1.385(3)		

Bond angles			
C(30)-Co(1)-C(31)	103.30(10)	C(30)-Co(1)-C(37)	100.25(10)
C(31)-Co(1)-C(37)	142.83(9)	C(30)-Co(1)-P(1)	92.05(7)
C(31)-Co(1)-P(1)	98.02(7)	C(37)-Co(1)-P(1)	109.50(6)
C(30)-Co(1)-Co(2)	148.48(7)	C(31)-Co(1)-Co(2)	102.00(7)
C(37)-Co(1)-Co(2)	48.66(6)	P(1)-Co(1)-Co(2)	102.721(16)
C(30)-Co(1)-Co(3)	97.61(7)	C(31)-Co(1)-Co(3)	98.69(7)
C(37)-Co(1)-Co(3)	49.59(6)	P(1)-Co(1)-Co(3)	158.196(18)
Co(2)-Co(1)-Co(3)	60.021(10)	C(36)-Co(2)-C(35)	103.93(12)
C(36)-Co(2)-C(37)	107.59(10)	C(35)-Co(2)-C(37)	140.13(9)
C(36)-Co(2)-P(2)	93.69(8)	C(35)-Co(2)-P(2)	101.94(7)
C(37)-Co(2)-P(2)	99.78(6)	C(36)-Co(2)-Co(1)	152.97(8)
C(35)-Co(2)-Co(1)	93.16(7)	C(37)-Co(2)-Co(1)	49.22(6)
P(2)-Co(2)-Co(1)	103.194(16)	C(36)-Co(2)-Co(3)	94.69(7)
C(35)-Co(2)-Co(3)	104.28(7)	C(37)-Co(2)-Co(3)	49.86(6)
P(2)-Co(2)-Co(3)	149.591(19)	Co(1)-Co(2)-Co(3)	60.423(11)
C(32)-Co(3)-C(34)	94.56(10)	C(32)-Co(3)-C(33)	105.29(10)
C(34)-Co(3)-C(33)	103.30(11)	C(32)-Co(3)-C(37)	104.43(9)
C(34)-Co(3)-C(37)	102.86(10)	C(33)-Co(3)-C(37)	138.24(9)
C(32)-Co(3)-Co(2)	151.59(7)	C(34)-Co(3)-Co(2)	99.27(7)
C(33)-Co(3)-Co(2)	95.55(7)	C(37)-Co(3)-Co(2)	48.31(6)
C(32)-Co(3)-Co(1)	97.73(7)	C(34)-Co(3)-Co(1)	151.01(8)
C(33)-Co(3)-Co(1)	98.62(7)	C(37)-Co(3)-Co(1)	48.59(6)
Co(2)-Co(3)-Co(1)	59.555(11)	C(12)-P(1)-C(6)	103.34(9)
C(12)-P(1)-C(4)	102.26(9)	C(6)-P(1)-C(4)	102.55(9)
C(12)-P(1)-Co(1)	117.63(6)	C(6)-P(1)-Co(1)	109.98(7)
C(4)-P(1)-Co(1)	119.01(6)	C(24)-P(2)-C(5)	100.69(9)
C(24)-P(2)-C(18)	103.36(9)	C(5)-P(2)-C(18)	104.97(8)
C(24)-P(2)-Co(2)	120.67(6)	C(5)-P(2)-Co(2)	112.88(6)

C(18)-P(2)-Co(2)	112.51(6)	O(1)-C(1)-C(2)	125.91(18)
O(1)-C(1)-C(5)	126.46(18)	C(2)-C(1)-C(5)	107.61(16)
C(1)-C(2)-C(3)	104.40(16)	O(2)-C(3)-C(2)	126.43(18)
O(2)-C(3)-C(4)	125.88(18)	C(2)-C(3)-C(4)	107.54(16)
C(5)-C(4)-C(3)	109.14(16)	C(5)-C(4)-P(1)	126.36(14)
C(3)-C(4)-P(1)	124.37(14)	C(4)-C(5)-C(1)	109.81(16)
C(4)-C(5)-P(2)	124.60(14)	C(1)-C(5)-P(2)	125.48(14)
C(11)-C(6)-C(7)	118.91(19)	C(11)-C(6)-P(1)	120.68(16)
C(7)-C(6)-P(1)	120.35(16)	C(8)-C(7)-C(6)	120.3(2)
C(9)-C(8)-C(7)	120.0(3)	C(10)-C(9)-C(8)	120.3(2)
C(9)-C(10)-C(11)	120.0(2)	C(6)-C(11)-C(10)	120.3(2)
C(13)-C(12)-C(17)	118.66(19)	C(13)-C(12)-P(1)	119.70(15)
C(17)-C(12)-P(1)	121.62(15)	C(14)-C(13)-C(12)	120.2(2)
C(15)-C(14)-C(13)	120.2(2)	C(14)-C(15)-C(16)	120.0(2)
C(15)-C(16)-C(17)	120.5(2)	C(16)-C(17)-C(12)	120.4(2)
C(23)-C(18)-C(19)	118.85(18)	C(23)-C(18)-P(2)	122.33(16)
C(19)-C(18)-P(2)	118.80(15)	C(20)-C(19)-C(18)	120.5(2)
C(21)-C(20)-C(19)	120.0(2)	C(22)-C(21)-C(20)	120.1(2)
C(21)-C(22)-C(23)	120.4(2)	C(18)-C(23)-C(22)	120.1(2)
C(25)-C(24)-C(29)	118.31(19)	C(25)-C(24)-P(2)	118.67(16)
C(29)-C(24)-P(2)	122.98(15)	C(26)-C(25)-C(24)	120.2(2)
C(27)-C(26)-C(25)	120.9(2)	C(26)-C(27)-C(28)	119.7(2)
C(27)-C(28)-C(29)	120.3(2)	C(28)-C(29)-C(24)	120.5(2)
O(3)-C(30)-Co(1)	179.4(2)	O(4)-C(31)-Co(1)	177.3(2)
O(5)-C(32)-Co(3)	176.4(2)	O(6)-C(33)-Co(3)	177.83(19)
O(7)-C(34)-Co(3)	177.1(2)	O(8)-C(35)-Co(2)	178.1(2)
O(9)-C(36)-Co(2)	179.2(2)	Co(2)-C(37)-Co(1)	82.12(8)
Co(2)-C(37)-Co(3)	81.83(8)	Co(1)-C(37)-Co(3)	81.82(8)

F. X-ray Diffraction Structure of P-C Bond Cleavage Compound (5)

Single crystals of compound **5** were grown from a CH_2Cl_2 solution containing **5** that had been layered with heptane. The X-ray data collection and processing parameters for **5** was given in Table 2.1, with the selected bond distances and angles given in Table 3.5 and Table 3.6. The ORTEP diagram is shown in Figure 3.9.

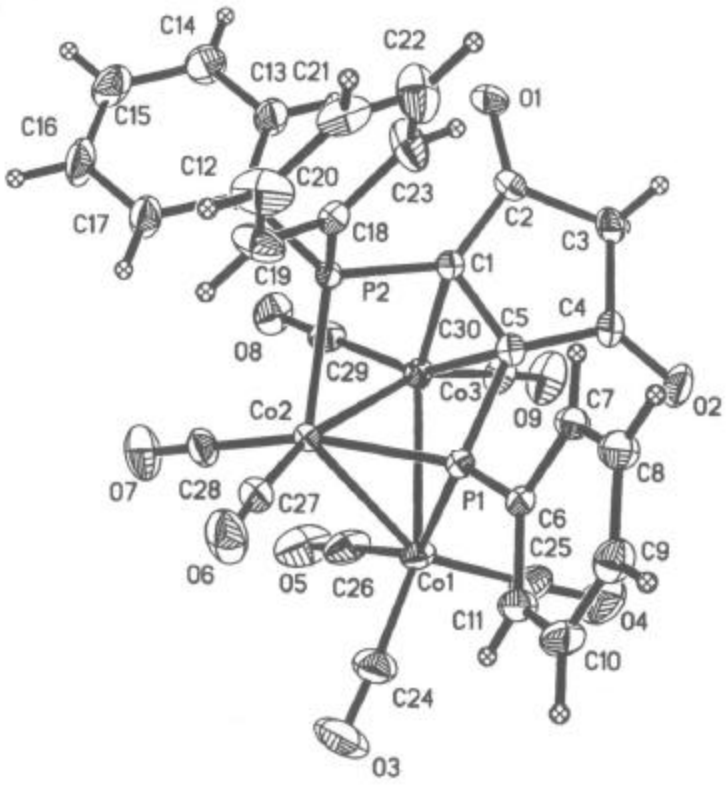


Figure 3.9 The ORTEP diagram of the P-C bond cleavage compound **(5)**

Table 3.5 Positional parameters for the non-hydrogen atoms in the P-C bond cleavage compound **(5)** with estimated standard deviations in parentheses

atom	x ($x10^4$)	y ($x10^4$)	z ($x10^4$)	B, ($Å^2 x 10^3$)
Co(1)	6828(1)	1092(1)	897(1)	36(1)
Co(2)	4809(1)	871(1)	1733(1)	27(1)
Co(3)	4380(1)	1186(1)	-897(1)	28(1)
P(1)	5585(1)	1471(1)	1792(2)	27(1)
P(2)	2727(1)	1108(1)	940(1)	24(1)
O(1)	854(4)	1760(1)	-2054(5)	41(1)
O(2)	5268(5)	2300(1)	-333(6)	54(1)
O(3)	8852(8)	785(2)	3643(9)	89(2)
O(4)	8139(7)	1715(2)	-365(9)	90(2)
O(5)	6581(7)	395(2)	-1136(9)	88(2)
O(6)	5664(8)	761(2)	5049(6)	67(2)
O(7)	4606(8)	31(1)	708(8)	72(2)
O(8)	3128(6)	470(1)	-2582(6)	58(1)
O(9)	4969(7)	1536(2)	-3530(7)	71(2)
C(1)	2968(5)	1518(1)	-277(5)	25(1)
C(2)	2075(6)	1785(2)	-1453(5)	29(1)
C(3)	2925(7)	2130(2)	-1745(6)	37(1)
C(4)	4309(6)	2077(2)	-555(7)	36(1)
C(5)	4276(6)	1704(1)	309(5)	27(1)
C(6)	6099(5)	1799(1)	3434(6)	28(1)
C(7)	5212(6)	2101(2)	3598(7)	35(1)
C(8)	5562(7)	2335(2)	4908(7)	42(1)
C(9)	6788(8)	2277(2)	6046(7)	45(1)
C(10)	7670(7)	1992(2)	5876(8)	45(1)
C(11)	7333(6)	1755(2)	4567(7)	39(1)

C(12)	1400(5)	763(2)	-136(6)	31(1)
C(13)	404(7)	860(2)	-1467(8)	47(1)
C(14)	-566(8)	580(2)	-2231(10)	62(2)
C(15)	-550(8)	200(2)	-1623(10)	60(2)
C(16)	441(9)	100(2)	-288(10)	63(2)
C(17)	1400(8)	381(2)	464(8)	53(2)
C(18)	2024(5)	1332(2)	2336(6)	28(1)
C(19)	2139(8)	1137(3)	3707(8)	57(2)
C(20)	1565(9)	1316(3)	4725(8)	67(2)
C(21)	908(7)	1676(2)	4418(7)	47(2)
C(22)	793(10)	1862(2)	3070(10)	63(2)
C(23)	1339(9)	1689(2)	2026(8)	52(2)
C(24)	8092(8)	913(2)	2563(10)	57(2)
C(25)	7646(8)	1467(2)	111(9)	55(2)
C(26)	6644(7)	669(2)	-370(9)	57(2)
C(27)	5302(7)	792(2)	3763(7)	40(1)
C(28)	4685(7)	349(2)	1121(8)	43(1)
C(29)	3615(6)	745(2)	-1896(7)	39(1)
C(30)	4718(7)	1411(2)	-2501(7)	41(1)

Table 3.6 Selected bond distances (Å) and angles (deg) for the P-C bond cleavage compound **(5)**

Bond distances			
Co(1)-C(24)	1.776(8)	Co(1)-C(25)	1.785(7)
Co(1)-C(26)	1.797(7)	Co(1)-P(1)	2.1462(14)
Co(1)-Co(2)	2.5620(10)	Co(1)-Co(3)	2.5755(11)
Co(2)-C(27)	1.793(6)	Co(2)-C(28)	1.813(6)
Co(2)-P(1)	2.1463(13)	Co(2)-P(2)	2.1986(15)
Co(2)-Co(3)	2.5441(9)	Co(3)-C(29)	1.777(6)
Co(3)-C(30)	1.786(5)	Co(3)-C(1)	2.055(5)
Co(3)-C(5)	2.069(4)	P(1)-C(5)	1.771(5)
P(1)-C(6)	1.802(5)	P(2)-C(18)	1.825(5)
P(2)-C(12)	1.824(5)	P(2)-C(1)	1.831(5)
O(1)-C(2)	1.216(7)	O(2)-C(4)	1.206(7)
O(3)-C(24)	1.138(10)	O(4)-C(25)	1.129(9)
O(5)-C(26)	1.142(8)	O(6)-C(27)	1.128(8)
O(7)-C(28)	1.116(8)	O(8)-C(29)	1.135(7)
O(9)-C(30)	1.138(7)	C(1)-C(5)	1.435(7)
C(1)-C(2)	1.477(7)	C(2)-C(3)	1.522(7)
C(3)-C(4)	1.517(9)	C(4)-C(5)	1.479(7)
C(6)-C(11)	1.380(8)	C(6)-C(7)	1.402(7)
C(7)-C(8)	1.384(8)	C(8)-C(9)	1.382(10)
C(9)-C(10)	1.361(9)	C(10)-C(11)	1.388(9)
C(12)-C(13)	1.368(9)	C(12)-C(17)	1.386(8)
C(13)-C(14)	1.390(9)	C(14)-C(15)	1.377(11)
C(15)-C(16)	1.371(12)	C(16)-C(17)	1.381(10)
C(18)-C(23)	1.367(8)	C(18)-C(19)	1.389(8)
C(19)-C(20)	1.394(10)	C(20)-C(21)	1.362(12)
C(21)-C(22)	1.357(11)	C(22)-C(23)	1.388(8)

Bond angles			
C(24)-Co(1)-C(25)	105.4(4)	C(24)-Co(1)-C(26)	101.3(4)
C(25)-Co(1)-C(26)	104.4(3)	C(24)-Co(1)-P(1)	103.6(2)
C(25)-Co(1)-P(1)	99.7(2)	C(26)-Co(1)-P(1)	139.0(2)
C(24)-Co(1)-Co(2)	95.6(3)	C(25)-Co(1)-Co(2)	149.7(3)
C(26)-Co(1)-Co(2)	92.4(2)	P(1)-Co(1)-Co(2)	53.36(4)
C(24)-Co(1)-Co(3)	154.7(3)	C(25)-Co(1)-Co(3)	99.0(3)
C(26)-Co(1)-Co(3)	78.4(3)	P(1)-Co(1)-Co(3)	65.31(4)
Co(2)-Co(1)-Co(3)	59.37(3)	C(27)-Co(2)-C(28)	98.8(3)
C(27)-Co(2)-P(1)	97.32(18)	C(28)-Co(2)-P(1)	152.2(2)
C(27)-Co(2)-P(2)	108.9(2)	C(28)-Co(2)-P(2)	105.9(2)
P(1)-Co(2)-P(2)	89.86(5)	C(27)-Co(2)-Co(3)	163.17(18)
C(28)-Co(2)-Co(3)	97.2(2)	P(1)-Co(2)-Co(3)	65.91(4)
P(2)-Co(2)-Co(3)	71.32(4)	C(27)-Co(2)-Co(1)	111.3(2)
C(28)-Co(2)-Co(1)	99.5(2)	P(1)-Co(2)-Co(1)	53.35(4)
P(2)-Co(2)-Co(1)	127.67(4)	Co(3)-Co(2)-Co(1)	60.58(3)
C(29)-Co(3)-C(30)	95.2(3)	C(29)-Co(3)-C(1)	110.1(2)
C(30)-Co(3)-C(1)	110.5(2)	C(29)-Co(3)-C(5)	150.7(2)
C(30)-Co(3)-C(5)	98.8(2)	C(1)-Co(3)-C(5)	40.7(2)
C(29)-Co(3)-Co(2)	93.8(2)	C(30)-Co(3)-Co(2)	159.7(2)
C(1)-Co(3)-Co(2)	83.21(13)	C(5)-Co(3)-Co(2)	81.72(13)
C(29)-Co(3)-P(1)	143.3(2)	C(30)-Co(3)-P(1)	118.5(2)
C(1)-Co(3)-P(1)	73.06(14)	C(5)-Co(3)-P(1)	43.17(15)
Co(2)-Co(3)-P(1)	49.59(3)	C(29)-Co(3)-Co(1)	114.9(2)
C(30)-Co(3)-Co(1)	99.6(2)	C(1)-Co(3)-Co(1)	122.29(14)
C(5)-Co(3)-Co(1)	88.05(16)	Co(2)-Co(3)-Co(1)	60.05(3)
P(1)-Co(3)-Co(1)	49.27(3)	C(29)-Co(3)-P(2)	88.64(18)
C(30)-Co(3)-P(2)	149.8(2)	C(1)-Co(3)-P(2)	41.19(13)
C(5)-Co(3)-P(2)	66.68(13)	Co(2)-Co(3)-P(2)	48.54(3)
P(1)-Co(3)-P(2)	69.85(4)	Co(1)-Co(3)-P(2)	105.92(4)
C(5)-P(1)-C(6)	109.4(2)	C(5)-P(1)-Co(2)	101.34(17)
C(6)-P(1)-Co(2)	126.36(16)	C(5)-P(1)-Co(1)	111.69(16)
O(6)-P(1)-Co(1)	128.48(18)	Co(2)-P(1)-Co(1)	73.29(4)

C(5)-P(1)-Co(3)	53.07(15)	C(6)-P(1)-Co(3)	162.48(18)
Co(2)-P(1)-Co(3)	64.50(4)	Co(1)-P(1)-Co(3)	65.42(4)
C(18)-P(2)-C(12)	103.6(2)	C(18)-P(2)-C(1)	106.9(2)
C(12)-P(2)-C(1)	111.2(2)	C(18)-P(2)-Co(2)	118.97(18)
C(12)-P(2)-Co(2)	116.74(17)	C(1)-P(2)-Co(2)	99.11(17)
C(18)-P(2)-Co(3)	148.53(16)	C(12)-P(2)-Co(3)	103.61(15)
C(1)-P(2)-Co(3)	47.67(14)	Co(2)-P(2)-Co(3)	60.14(4)
C(5)-C(1)-C(2)	108.4(4)	C(5)-C(1)-P(2)	112.9(4)
C(2)-C(1)-P(2)	136.0(4)	C(5)-C(1)-Co(3)	70.2(3)
C(2)-C(1)-Co(3)	117.2(3)	P(2)-C(1)-Co(3)	91.1(2)
O(1)-C(2)-C(1)	127.9(5)	O(1)-C(2)-C(3)	123.5(5)
C(1)-C(2)-C(3)	108.4(5)	C(4)-C(3)-C(2)	104.9(4)
O(2)-C(4)-C(5)	125.6(6)	O(2)-C(4)-C(3)	126.6(5)
C(5)-C(4)-C(3)	107.8(4)	C(1)-C(5)-C(4)	109.9(5)
C(1)-C(5)-P(1)	120.3(3)	C(4)-C(5)-P(1)	129.7(4)
C(1)-C(5)-Co(3)	69.1(2)	C(4)-C(5)-Co(3)	113.3(3)
P(1)-C(5)-Co(3)	83.77(19)	C(11)-C(6)-C(7)	118.7(5)
C(11)-C(6)-P(1)	121.8(4)	C(7)-C(6)-P(1)	119.5(4)
C(8)-C(7)-C(6)	119.7(5)	C(9)-C(8)-C(7)	120.4(6)
C(10)-C(9)-C(8)	120.2(6)	C(9)-C(10)-C(11)	120.1(6)
C(6)-C(11)-C(10)	120.9(5)	C(13)-C(12)-C(17)	118.5(6)
C(13)-C(12)-P(2)	124.4(4)	C(17)-C(12)-P(2)	117.1(5)
C(12)-C(13)-C(14)	121.1(6)	C(15)-C(14)-C(13)	119.7(7)
C(16)-C(15)-C(14)	119.7(7)	C(15)-C(16)-C(17)	120.1(6)
C(16)-C(17)-C(12)	120.8(7)	C(23)-C(18)-C(19)	118.8(5)
C(23)-C(18)-P(2)	120.3(4)	C(19)-C(18)-P(2)	120.8(4)
C(18)-C(19)-C(20)	118.7(7)	C(21)-C(20)-C(19)	121.9(6)
C(22)-C(21)-C(20)	118.9(5)	C(21)-C(22)-C(23)	120.5(7)
C(18)-C(23)-C(22)	121.1(6)	O(3)-C(24)-Co(1)	176.3(9)
O(4)-C(25)-Co(1)	177.4(7)	O(5)-C(26)-Co(1)	177.1(8)
O(6)-C(27)-Co(2)	176.0(6)	O(7)-C(28)-Co(2)	178.2(6)
O(8)-C(29)-Co(3)	177.5(6)	O(9)-C(30)-Co(3)	176.4(6)

Chapter References

1. Bott, S. G.; Shen, H.; Richmond, M. G. *Struc. Chem.* **2001**, 12, 225.
2. (a) Kolle, U. *J. Organomet. Chem.* **1977**, 133, 53. (b) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev*. **1984**, 53, 227.
3. (a) Xia, C.-G.; Bott, S. G.; Richmond, M. G. *Inorg. Chim. Acta* **1995**, 230, 45. (b) Shen, H.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 4625. (c) Shen, H.; Bott, S. G.; Richmond, M. G. *J. Chem. Crystallogr*. **1998**, 28, 385.
4. (a) Garrou, P. E. *Chem. Rev*. **1981**, 81, 229. (b) Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, 19, 1277.
5. (a) Schulman, C. L.; Richmond, M. G.; Watson, W. H.; Nagl, A. *J. Organomet. Chem*. **1989**, 368, 367. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, 6, 254.

Chapter IV Discussion

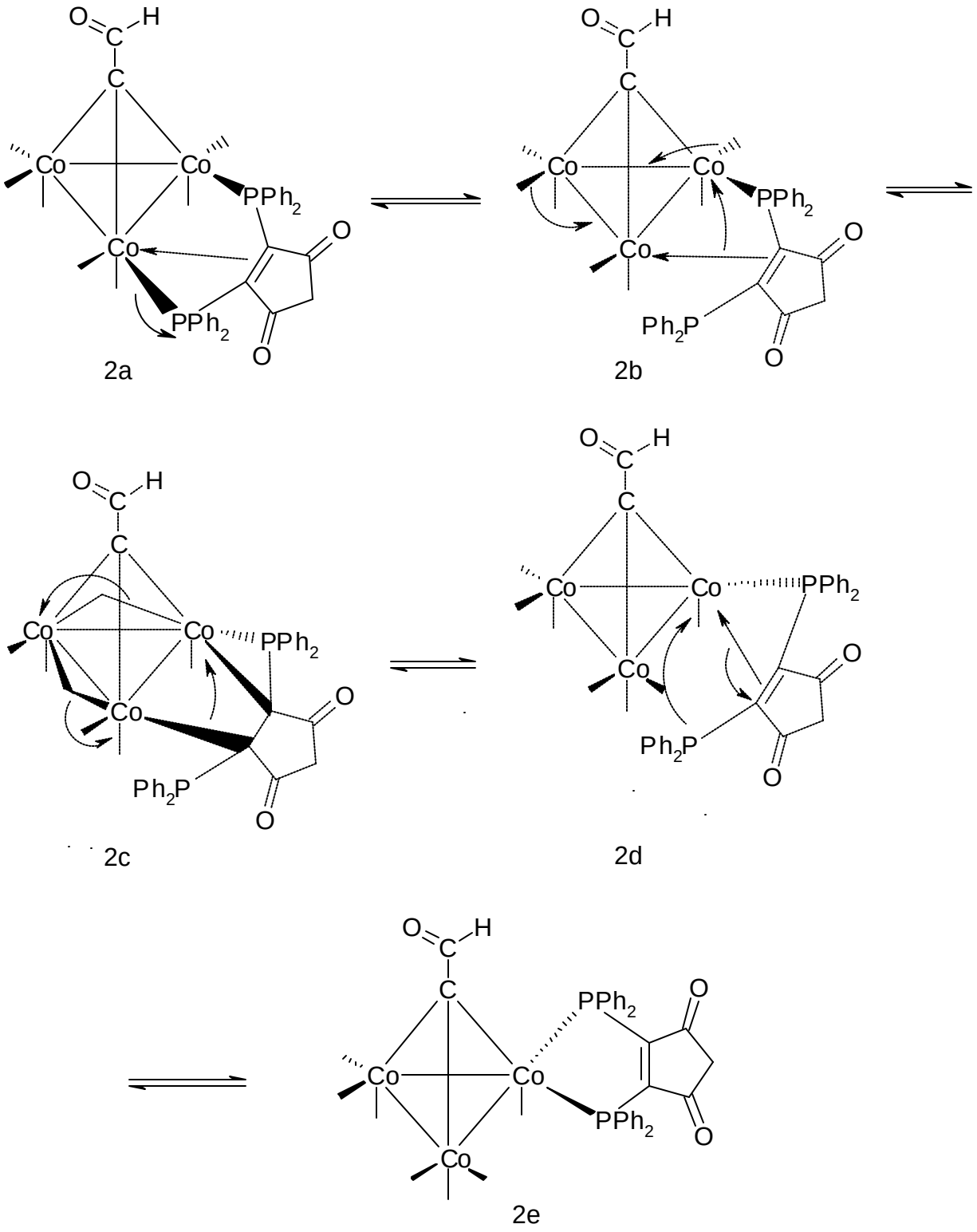
A. Syntheses for 2 and 4

The reaction of $OHCCCo_3(CO)_9$ with the bidentate ligand bpcd in the presence of Me_3NO proceeds initially to give the diphosphine cluster $OHCCCo_3(CO)_7$(bpcd). Variable-temperature ^{31}P NMR measurements indicate that this cluster exists as a mixture of bridging and chelating isomers.[1] As examined at 187 K, the bridging and chelating isomer have been found to be present in the same amount in solution by ^{31}P NMR spectroscopy. At 187 K the bridging isomer of $OHCCo_3(CO)_7$(bpcd) exhibits two phosphine resonances due to two different conformations of the bpcd ligand relative to the tricobalt core. Here the bpcd ligand is axially disposed (~10%) and equatorially bound. X-ray diffraction analysis reveals that the solid-state structure is derived from the chelating isomer.

The noncoordinated C=C double bond of the cyclopentene ring is believed to facilitate the observed bridge-to-chelate equilibration process that is outlined in Scheme 4.1.[2] Starting with the bridged isomer, **2a**, and invoking a unimolecular mechanism that does not rely on CO loss, phosphine ligand displacement by the cyclopentene C=C bond affords the saturated cluster **2b**. Assuming that the coordinated olefinic in species **2b** behaves similarly as a CO ligand in terms of migratory ability, an in-plane migration of two equatorial CO groups and the olefin moiety leads to cluster **2c** with a bridging olefinic bond. Completion of the terminal-to-bridge ligand migration then yields the chelated alkenyl phosphine cluster **2d**, which, upon olefin displacement by the free,

dangling PPh_2 moiety, gives the chelating diphosphine cluster **2e**. It is this chelating isomer, which its two identical equatorial PPh_2 groups, along with two bridging isomers of **2**, that were observed in the low-temperature ^{31}P NMR spectra of **2**. The determined X-ray structure of **2** is identical with the proposed isomer **2e**.

The proposed bpcd ligand equilibration is consistent with the fact that terminal/bridge CO exchange is known to be facile in this type of cluster and our previous work reported with the bma ligand has shown a similar P-ligand movement.[2] The main point of difference lies in the fact that the bma ligand prefers to adopt an axial and equatorial PPh_2 in the chelating isomer, while our work shows two identical equatorial PPh_2 groups.



Scheme 4.1

B. X-ray Diffraction Structures of 2, 4 and 5

Single crystals of **2**, **4**, and **5** were grown, and the molecular structure of each cluster was determined.

The ORTEP diagram of **2** establishes the chelating disposition of the bpcd ligand. The polyhedral core of **2** consists of a triangular array of cobalt atoms capped by a μ_3-CR moiety. Unequal Co-Co bond lengths are seen in **2**, with the bpcd-substituted Co(1)-Co(2) (2.4944Å), Co(1)-Co(3) (2.4933Å) bonds being slightly longer than the Co(2)-Co(3) (2.4923Å) bond. The reason for this difference can be attributed to a sterically induced perturbation of the cluster core by the bpcd ligand. The mean value for the μ_3-C-Co bonds (1.913Å) is consistent with those reported for related clusters.[3] The bpcd attached C(36)-Co(1) (1.884Å) bond is shorter than the other two bonds C(36)-Co(2) (1.921Å) and C(36)-Co(3) (1.933Å), and this observation is consistent with our assumption that bpcd can work as a good electron reservior. The Co-CO (1.702Å) distances are consistent with those reported[3] for related clusters with the exception of Co(2)-C(31) (1.834Å), which is much longer than the others. From the ORTEP diagram, we can see that this bond is in the same plane of CHO group, but it takes the opposite direction of CHO. The remaining distances and angles are unexceptional and require no comment.

The Co-Co bond distances in cluster **4** range from 2.4720 to 2.4937Å, with a mean distance of 2.4831 Å, the bpcd-substituted Co(1)-Co(2) bond (2.4720Å) is shorter than the other two cobalt bonds Co(1)-Co(3) (2.4937Å) and Co(2)-Co(3) (2.4837Å). This

supports the greater electron donations of the bpcd ligand relative to the CO group. The mean value for the μ_3-C-Co bonds (1.8938Å) is consistent with those reported for related clusters. The C(37)-Co(3) bond (1.9182Å) bond which is not attached to bpcd is longer than the other two bonds C(37)-Co(1) (1.8896Å) and C(37)-Co(2) (1.8736Å). This observation is consistent with our assumption that the bpcd interacts with tricobalt cluster and makes the attached bonds more electron rich, which leads to a bond lengthening. All other bond distances and angles are within normal limits and require no comment.

The Co-Co bond distances in cluster **5** are 2.5620 Å, 2.5441 Å, and 2.5755 Å, with a mean distance of 2.5605 Å. A mean distance of 2.1637 Å has been observed for the Co-P bonds. The bond distances of C(1)-Co(3) (2.055Å) and C(5)-Co(3) (2.069Å) are little longer than the normal C-Co bonds(1.90Å), that consistent with the assumption that this C=C double bond is coordinated to the cobalt atom. All other bond distances and angles are within normal limits and require no comment.

Chapter References

1. (a) Schulman, C. L.; Richmond, M. G.; Watson, W. H.; Nagl, A. *J. Organomet. Chem.* **1989**, 368, 367. (b) Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, 6, 254.
2. Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 2718.
3. (a) Colbran, S. B.; Robinson, B.; Simpson, J. *Acta Crystallogr.* **1986**, C42, 972. (b) Ahlgrén, M.; Pakkanen, T. T.; Tahvanainen, I. *J. Organomet. Chem.* **1987**, 323, 91. (c) Aitchison, A. A.; Farrugia, L. J. *Organometallics* **1987**, 6, 819. (d) Brice, M. D.; Penfold, B. R.; Robinson, W. T.; Taylor, S. R. *Inorg. Chem.* **1970**, 9, 362.

Reference List

Ahlgrén, M.; Pakkanen, T. T.; Tahvanainen, I. *J. Organomet. Chem.* **1987**, 323, 91.

Aitchison, A. A.; Farrugia, L. J. *Organometallics* **1987**, 6, 819.

Albers, M. O.; Coville, N. J. *Coord. Chem. Rev*. **1984**, 53, 227.

Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, 26, 343.

Arewgoda, M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *J. Am. Chem. Soc*. **1982**, 104, 5633.

Balavoine, G.; Collin, J.; Bonnet, J. J.; Lavigne, G. *J. Organomet. Chem.* **1985**, 280, 429.

Becher, H. J.; Bensmann, W.; Fenske, D. *Chem. Ber*. **1977**, 110, 315.

Bennett, M. J.; Donaldson, P. B. *Inorg.* Chem. **1977**, 16, 655.

Bensmann, W.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 462.

Bensmann, W.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 677.

Bott, S. G.; Shen, H.; Richmond, M. G. *Struc. Chem.* **2001**, 12, 225.

Brice, M. D.; Penfold, B. R.; Robinson, W. T.; Taylor, S. R. *Inorg. Chem.* **1970**, 9, 362.

Brice, M. D.; Penfold, B. R.; Robinson, W. T.; Taylor, S. R. *Inorg. Chem.* **1970**, 9, 1457.

Bruce, M. I.; Hambley, T. W.; Nicholson, B. K.; Rieger, P. H.; Williams, R. L. *J. Chem. Soc., Chem. Commun.* **1982**, 442.

Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, 247, 321.

Cetin, G.; Ercoli, R.; Gambino, O.; Vaglio, G. *Atti. Accad. Sci. Torino, Cl. Sci. Fis. Mat. Natur*. **1964**, 99, 1123.

Churchill, M. R.; Lashewycz, R. A.; Shapley, J. R.; Richter, S. I. *Inorg. Chem.* **1980**, 19, 1277.

Clark, H. C. *Isr. J. Chem.* **1976/77**, 15, 210.

Colbran, S. B.; Robinson, B.; Simpson, J. *Acta Crystallogr.* **1986**, C42, 972.

Collin, J.; Jossart, C.; Balavoine, G. *Organometallics* **1986**, 5, 203.

Collman, J.P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *"Principles and Applications of Organotransition metal Chemistry."* University Science Books, Mill Valley, CA, **1987**, chapter 2.

Darensbourg, D.; Bischoff, C. J. *Inorg. Chem.* **1993**, 32, 47.

Davies, J. A.; In *"The Chemistry of the Metal-Carbon Bond"* Hartley, F. R.; Ed; Wiley-Interscience, New York, **1982**, chapter 21, p880.

Fenske, D. *Angew. Chem., Intl. Ed. Engl.* **1976**, 15, 381.

Fenske, D. *Chem. Ber.* **1979**, 112, 363.

Fenske, D.; Becher, H. J. *Chem. Ber.* **1974**, 107, 117.

Fenske, D.; Becher, H. J. *Chem.. Ber*. **1975**, 108, 2115.

Fenske, D.; Christidis, A. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 129.

Garrou, P. E. *Chem. Rev.* **1981**, 81, 229.

Hegedus, L. S. *Coord. Chem. Rev*. **2000**, 204, 199.

Hitchcock, P. B.; McPartlin, M.; Mason, R. *Chem. Commun*. **1969**, 1367.

Kofen, W. G.; Backlawski, L. M. *J. Org. Chem.* **1976**, 41, 1879.

Kolle, U. *J. Organomet. Chem.* **1977**, 133, 53.

Levason, W.; McAuliffe, C. A. *Acc. Chem. Res.* **1978**, 11, 363.

Levason, W.; McAuliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1972**, 14, 173.

Mao, F.; Philbin, C. E.; Weakley, T. J. R.; Tyler, D. R. *Organometallics*, **1990**, 9, 1510.

Mao, F.; Sur, S. K.; Tyler, D. R. *Organometallics*, **1991**, 10, 419.

Mao, F.; Tyler, D. R.; Bruce, M. R. M.; Bruce, A. E.; Rieger, A. L.; Rieger, P. H. *J. Am. Chem. Soc.* **1992**, 114, 6418.

Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, 111, 130.

Mao, F.; Tyler, D. R.; Rieger, A. L.; Rieger, P. H. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 3113.

Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc.* **1971**, A, 1457.

McAuliffe, C. A. *"Transition-Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands."* Wiley, New York, **1973**.

McBee, E. T.; Meyers, R. K.; Baranauckas, C. F. *J. Am. Chem. Soc.* **1955**, 77, 86.

Morris, R. J.; Girolami, G. S. *Inorg. Chem.* **1990**, 29, 4167.

Nestle, M. O.; Hallgren, J. E.; Seyferth, D. *Inorg. Synth.* **1980**, 20, 226.

Omae, I. *"Applications of Organometallic Compounds."* John Wiley & Sons, New York, NY, **1998**, Chapter 17.

Orpen, A.G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310.

Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, 6, 73.

Pregosin, P. S.; Kunz, R. W. In *"NMR Basic Principles and Progress"* Springer-Verlag, Heidelberg, **1979**, Vol 16, p55.

Richmond, M. G.; Kochi, J. K. *Organometallics* **1987**, 6, 254.

Roedig, A.; Hörnig, L. *Chem. Ber.* **1955**, 88, 2003.

Schulman, C. L.; Richmond, M. G.; Watson, W. H.; Nagl, A. *J. Organomet. Chem.* **1989**, 368, 367.

Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, 16, 758.

Shen, H.; Bott, S. G.; Richmond, M. G. *J. Chem. Crystallogr*. **1998**, 28, 385.

Shen, H.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 4625.

Shen, H.; Bott, S.G.; Richmond, M.G. *Inorg. Chim. Acta* **1996**, 241, 71.

Spek, A. L. *Acta Crystallogr*. **1982**, 29, 203.

Sutin, K. A.; Kolig, J. W.; Mlekuz, M.; Bougeard, P.; Ssayer, B. G.; Quilliam, M. A.; Faggium, R.; Lock, C. J. L.; McGlinchey, M. J.; Jaouen, G. *J. Organomet. Chem.* **1993**, 445, 163.

TEXSAN-TEXRAY *Structure Analysis Package;* Molecular Structure Corporation, Vers. 1.7-1, March **1995**.

Thimmappa, B. H. S. *Coord. Chem. Rev*. **1995**, 143, 1.

Tolman, C.A. *Chem. Rev*. **1977**, 77, 313.

Tyler, D. R. *Acc. Chem. Res.* **1991**, 24, 325.

Xia, C.-G.; Bott, S. G.; Richmond, M. G. *Inorg. Chim. Acta* **1995**, 230, 45.

Xia, C.-G.; Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1996,** 15, 4480.

Xiao, S.-X.; Trogler, W. C.; Ellis, D.E.; Berkovitch-Yellin, Z. J. *J. Am. Chem. Soc.* **1983**, 105, 7033.

Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 2718.

Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, 14, 2387.